ARSENIC

ANNUAL SURVEY COVERING THE YEARS 1976 AND 1977

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I. Introduction

The purpose of this review is to cover the recent literature which has been published in the field of organoarsenic chemistry. Specifically, those

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* Arsenic, Annual Survey covering the year 1975 see J. Organometal. Chem., Vol. 138 (1977) p. 125-156.

publications are included which have been abstracted in volumes 84, 85, 86, and 87 of Chemical Abstracts. As has been the case in recent years, a large number of publications have appeared which are concerned with the preparation and characterization of transition metal complexes in which arsines function as the donor molecules. The bulk of these papers is not included in this review as they are considered to belong to the field of transition metal coordination chemistry rather than organoarsenic chemistry. In some cases, when an unusual ligand has been synthesized, or a unique complex bearing a transition metal-arsenic bond has been studied, such papers are included in this review.

The literature which is concerned with the environmental and biochemical aspects of organoarsenic compounds has also undergone a great increase in volume during the past several years. So much so, in fact, that only a selected number of papers in this area could be included in the present review. Although the selection was intended to be critical, it probably reflects in large degree the interests of the authors of this review. Nevertheless, the number of papers reviewed is considerable and this number is expected to increase rapidly in future years.

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II. Reviews and Books

A 332 page report entitled *Arsenic*, which is concerned primarily with the medical and biological effects of the element in the environment, has been published by the National Academy of Sciences [1]. The toxicology of environmental arsenic has also been reviewed by Fowler [2]. Chester [3] has prepared a review on environmental pollution by arsenic. Japanese reviews on the use of organoarsenicals against chick parasite diseases [4] and arsenic in foods [5] have appeared.

Duncan [6,7,8] has reported on recent developments in synthetic arsenic chemistry. The spectrophotometric methods for the determination of trace amounts of arsenic have been reviewed in considerable detail by Russian authors [9].

Hursthouse [10] has reviewed the structural data reported for several crystalline derivatives of arsenic and a very extensive report on the structural chemistry of organic derivatives of group Va elements has been published by Russian authors [11]. Reviews on the stereochemistry of tertiary arsines [12] and some coordination compounds of arsenic [13] have also appeared. Wardell [14] has reported on a number of organoarsenicals. The chemistry of heterocyclic arsenic compounds has been reviewed by Gallagher [15] while inorganic, five-membered ring systems containing both silicon and arsenic have been discussed by German authors [16]. Reviews have been published on the chemistry of arsino-oximes [17] and on the reactions of tertiary arsine oxides in the presence of alkyl halides [18].

III. Compounds Having a Metal-Arsenic Bond

Arsenic-boron bonded compounds have been prepared by three different synthetic techniques [19]. The first involves the reaction between a lithium diorganylarsenide and a boron halogen bond

$$R_2AsLi + ClBR'_2 \longrightarrow R_2As\text{-}BR'_2 + LiCl;$$

the second involves the reaction between a trimethylsilyl- or trimethylstannyl-arsine and a boron-halogen bonded compound,

$$(CH_3)_3E\text{-}As(CH_3)_2 + BrBRR' \longrightarrow (CH_3)_3EBr + (CH_3)_2As\text{-}BRR'$$
$$E = Sn,\ Si;$$

and the third involves the thermal rearrangement of a borane-diarsine adduct,

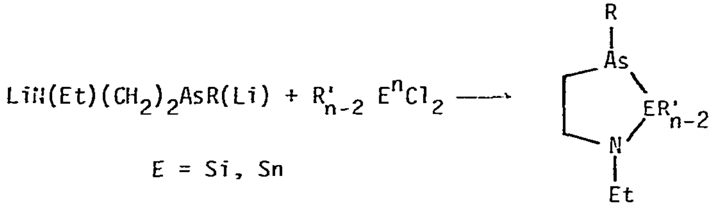
$$(CH_3)_2As\text{-}As(CH_3)_2\cdot BH_3 \longrightarrow (CH_3)_2AsH + (CH_3)_2AsBH_2.$$

Bis(amino)arsinoboranes are monomeric while $(C_6H_5)_2BAs(CH_3)_2$ is partially associated and decomposes readily. The compounds, $(CH_3)_2BAs(CH_3)_2$ and $(CH_3)_2AsBBrCH_3$ are trimeric. Trimeric and tetrameric forms of $(CH_3)_2AsBH_2$ were isolated.

Arsenic-silicon and arsenic-tin bonded derivatives have been prepared by Tzschach and Heinicke [20]. The reactions involved are shown below.

$$RNH(CH_2)_2As(C_6H_5)Li + Me_3SiCl \longrightarrow RNH(CH_2)_2As(C_6H_5)SiMe_3 + LiCl$$

$$2\ EtNH(CH_2)_2As(C_2H_5)H + (Bu_3Sn)_2O \longrightarrow 2\ EtNH(CH_2)_2As(Et)SnBu_3$$



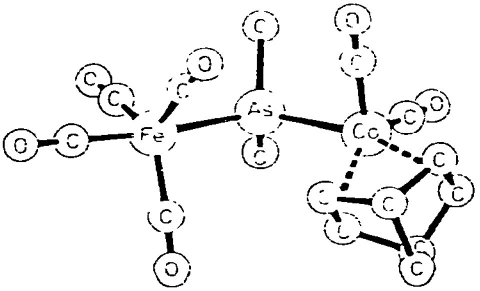
$LiN(Et)(CH_2)_2AsR(Li) + R'_{n-2}\ E^nCl_2 \longrightarrow$

$E = Si, Sn$

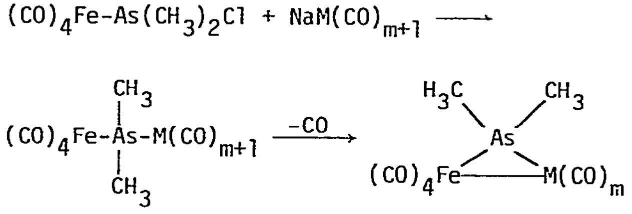
Diarsines form adducts with two moles of tin(IV) tetrahalides [21]. The tin-arsenic infrared bands were assigned as follows: Sn-As asymmetric stretch, 130 cm^{-1}; Sn-As symmetric stretch, 280 cm^{-1}; Sn-As bending vibration, 290 cm^{-1}. From Mössbauer spectra it was concluded that arsines are weaker donors toSn(IV) than either N- or O- ligands.

Demuth [22] and Beagley and Medwid [23] have reported on the structures of molecules bearing the Si-As bond. The As-Si fundamental stretching frequency is reported at 254 cm^{-1} in trifluorosilyldimethylarsine and at 346 cm^{-1} in $(SiH_3)_3As$. Electron diffraction studies of dimethyl(trifluorosilyl)arsine [24] show that the As-Si bond distance is 2.334 Å and the SiAsC bond angle is 93.5°. In $Cl_3SiAs(CH_3)_2$, the fundamentals As-Si stretching vibration has been observed by Demuth [25] at 324 cm^{-1}. Triorganostannylarsines have been reported to possess configurational stability within the NMR time scale [26], even in the presence of strong nucleophiles.

A large number of studies have been carried out in which the coordination of arsines to transition metal atoms has been reported. A few representative examples are the following. The reaction between $CoMn(CO)_9$ and $(CF_3)_2AsI$ yields the cobalt-arsenic bonded derivative, $(CF_3)_2AsCo(CO)_4$. The same compound is obtained by the reaction between *bis*(trifluoromethyl)arsine and dicobaltoctacarbonyl or from cobaltcarbonyl hydride and *bis*(trifluoromethyl)arsine. The fundamental arsenic-carbon stretching vibrations are reported at 734 and 726 cm^{-1} [27]. The structure of $(CF_3)_2AsCo(CO)_4$, as deduced from infrared data, is that of a trigonal bipyramid with an axial $(CF_3)_2As$ group. The crystal structure of $FeCo(CO)_7As(CH_3)_2$ has been determined by Keller and Vahrenkamp [28]. The Fe-As-Co triangle of the molecule is located on the crystallographic mirror plane. The triangle is unsymmetrical in shape with the bond lengths reported as follows: Fe-As = 2.33 Å, Co-As - 2.24 Å and Fe-Co - 2.70 Å. Four of the carbonyl groups are located around the iron atom and three around cobalt. The reaction of $(CO)_4Fe\text{-}As(CH_3)_2\text{-}Co(CO)_3$ with norbornadiene results in the displacement of two moles of carbon monoxide and the formation of the compound whose structure is shown below [29].



An interesting series of dinuclear complexes in which the dimethylarsino group functions as the bridging ligand has been prepared [30] according to the reaction shown in the equation which follows.



$$(CO)_4Fe\text{-}As(CH_3)_2Cl + NaM(CO)_{m+1} \longrightarrow$$

$$(CO)_4Fe\text{-}As(CH_3)_2\text{-}M(CO)_{m+1} \xrightarrow{-CO}$$

Examples of $M(CO)_{m+1}$ are $Mn(CO)_4$, $Re(CO)_4$, $Fe(CO)_2NO$ and $Co(CO)_3$. Examples of $M(CO)_m$ are $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_3NO$, and $Co(CO)_4$. Related studies describe compounds containing As-Ni [31], As-V [32] and As-Mo [33] bonds. The $AsMe_2$ group functions as a bridging ligand in the molecule

$$\pi\text{-}C_5H_5(CO)_3W\text{-}As(CH_3)_2\text{-}Ni(CO)_3$$

Based on values obtained from ^{51}V chemical shift parameters (τ), Rehder and Dorn using compounds of the type $[\eta^5\text{-CpV(CO)}_3L]$, arrange the ligands, L, as having the following Π-acceptor abilities:

$P(OR)_3 > CN^- > PR_3 \sim SbPh_3 \sim PPhF_2 > P(NR_2)_3 > PPh_3 > AsPh_3$. Mickiewicz and co-workers [33] describe the preparations of carbonyl anions of the type $[Mo(\eta\text{-}C_5H_5)(CO)_2L]^-$. When L is of a suitable type, e.g., $R_2AsCH_2CH_2CH_2Cl$, an anion is formed during the reduction process (sodium-amalgam) which undergoes reductive elimination with formation of five-membered molybdenum-arsenic rings.

IV. Compounds Having Arsenic-Nitrogen Bonds

A useful review by Kober [34] describes the synthesis, properties and molecular structures of aminoarsines. This report covers 175 published papers and discusses the nature and reactivity of the As-N bond and the application of aminoarsines in the synthesis of organoarsenic compounds.

Adler and Kobler have studied the following exchange using ^1H NMR spectroscopy [35].

$$(CH_3)_2As\text{-}^{14}N(CH_3)_2 + H^{15}N(CH_3)_2 \rightleftharpoons (CH_3)_2As\text{-}^{15}N(CH_3)_2 + H^{14}N(CH_3)_2$$

Above -60°, the exchange (in perdeuterotoluene as a solvent) is so rapid that all of the methyl protons attached to nitrogen atoms appear as a single NMR resonance. Below -60° the $HN(CH_3)_2$ and $=AsN(CH_3)_2$ methyl protons can be resolved.

Dimethylaminodifluoroarsine has been prepared according to the reaction shown in the equation which follows [36].

$$((CH_3)_3Si\text{-}N(CH_3)_2 + AsF_3 \rightarrow (CH_3)_3SiF + F_2As\text{-}N(CH_3)_2$$

The reaction between $[(C_6H_5)_4As]Cl$ and =N-lithium compounds has been studied by Russian workers [37]. The reaction of $(C_6H_5)_4As^+Cl^-$ with $LiNR_2$ gave $(C_6H_5)_3As$ and $C_6H_5NR_2$. With LiNHR, however, the reaction proceeded as follows.

$$(C_6H_5)_4As^+Cl^- + LiNHR \rightarrow [(C_6H_5)_4As\text{-}NHR] \rightarrow (C_6H_5)_3As{=}NR + C_6H_6$$

Russian workers have reported the results of a series of investigations concerned with asymmetric organoarsenic compounds with an arsenic-nitrogen bond [38-41]. The reactions employed and the types of compounds prepared are shown by the following equations:

$REtAsCl + NaNH_2 \rightarrow REtAsNH_2 + NaCl$

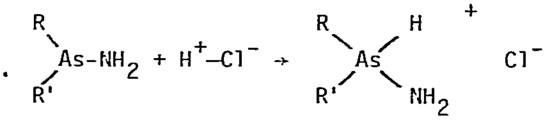
$EtAsRCl + 2HNR'_2 \rightarrow EtAsRNR'_2 + R_2NH_2^+Cl^-$

$R = C_6H_5$, *o*-, *m*-, *p*-tolyl, *o*-, *m*-, *p*-anisyl

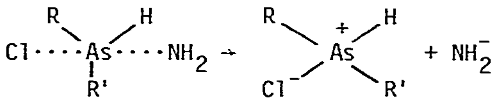
$R' = Et, Me$

NQR data (^{14}N, ^{35}Cl, ^{75}As) for $(Me_2N)_3As$, $(Me_2N)_2AsEt$, and Me_2NAsCl_2 have been obtained [41] and correlated with MO calculations (valence orbital populations).

Yambushev, *et al.*, [42] have reinvestigated the reaction of As-N bonded compounds with hydrogen chloride in ether. They interpret the reaction in terms of an S_N2 nucleophilic substitution mechanism. They propose a rapid first step in which the arsenic atom undergoes electrophilic attack by the proton.

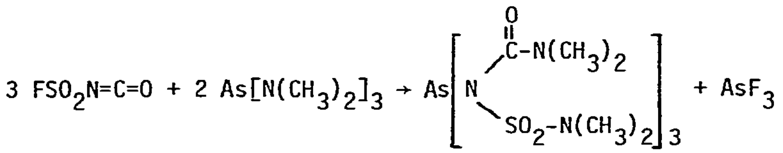


The next step proposed is the formation of a five-coordinate transition state intermediate followed by displacement of the amide by chloride.

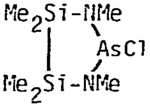


The final step involves the active hydrogen (≡As-H), the amide, and a second mole of HCl to form the haloarsine and the onium salt.

The reaction between *tris*(dimethylamino)arsine and fluorosulfonylisocyanate proceeds in a most interesting manner to produce AsF_3 and the compound shown in the equation [43].



The reaction between the N,N'-dilithio derivatives of 1,2-*bis*(methylamino)tetramethyldisilanes and $AsCl_3$ give five-membered heterocyclic derivatives of the type shown below [44]. The fundamental vibration,



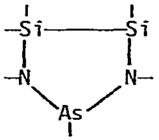
ν(As-Cl) is located at 388 cm^{-1} in these compounds. Krommes and Lorberth [45] have reported the preparation of a dimethylarsino-substituted diazomethane, $Me_2AsC(N)H_2$ by the reaction between dimethylaminodimethylarsine and a large excess of CH_2N_2 in the presence of Me_3SnCl. With $P(NMe_2)_3$ a 1-1 mixture of *cis*- and *trans*-*tris*(dimethylamino)-phosphine(dimethylarsinoformaldazine) is obtained.

$$Me_2AsCHN_2 + P(NMe_2)_3 \xrightarrow[Et_2O]{RT} Me_2AsC(H)=N-N=P(NMe_2)_3$$

The addition of diphenylarsine to the N=N double bond has been reported [46].

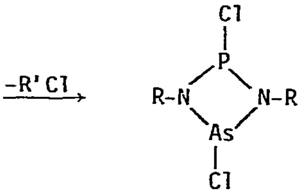
$$(C_6H_5)_2AsH + RN=NR \rightarrow (C_6H_5)_2As-N(R)-N(R)H$$

The formation of dimethylaminodimethylarsine by the reaction between *tris*(dimethyl amino)phosphine and glycol esters of arsenous acid has been reported by Kober [47] Some novel ring systems in which arsenic is bonded to nitrogen have been synthesized by Wannagat and Schlingmann (48]. Thus, *bis*(alkylamino)disilanes react with $AsCl_3$ to give the novel type of ring system shown below. Sherer and Schnabl [49] have

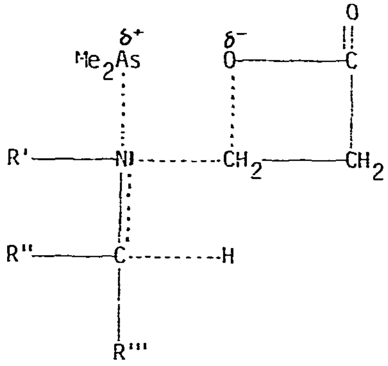


prepared some similar arsenic-phosphorus-nitrogen heterocycles. The reaction leading to the compound prepared by these investigators is given below.

$$RR'N-P=NR + AsCl_3 \rightarrow RR'N-PCl-NR-AsCl_2$$



Japanese workers [50] have carried out a kinetic study on the reaction of Me_2AsNR_2 with β-propiolactone. The reaction of N,N-dialkylamino-dimethylarsine with β-propiolactone gave dimethylarsino-3-dialkylaminopropionate. The reaction of aminoarsine is interpreted in terms of an ionic dipolar intermediate of the type shown below.



Arsenic containing polyamines have been prepared by Carraher and Moon [51]. They studied the condensation of triorganyldihaloarsines with diamines.

$$R_3AsX_2 + H_2N\text{-}R\text{-}NH_2 \rightarrow \{As(R_3)\text{-}N(H)\text{-}R\text{-}N(H)\}$$

The reactions between triphenylarsenic dichloride and nitro-p-phenylenediamine or trimethylarsenic dichloride (or dibromide) with the same amine were studied. The products exhibited weight-average molecular weights in the region of 10^5. A plastic crystalline phase has been reported for the *cage* arsenic-nitrogen bonded compound, *closo*-N-methylarsenimide, $As_4(NMe)_6$ [52]. This compound exhibits a large plastic range ($T_p = 346°$, $T_m = 393°K$).

V. Arsines and Polyarsines

The interest in the preparation and properties of transition metal complexes in which arsines function as Π-acceptor ligands continues unabated. As a consequence, new arsines and polyarsines are being synthesized. McAuliffe and coworkers have prepared a number of such arsenic-bearing ligands. The preparation of *cis*-2-diphenylarsinovinyldiphenylphosphine is carried out according to the following reaction sequence [53].

$$2\,Li + AsPh_3 \xrightarrow{THF} LiAsPh_2 + LiPh$$

$$LiPh + t\text{-}BuCl \longrightarrow LiCl + PhH + (CH_3)_2C{=}CH_2$$

$$LiAsPh_2 + \textit{cis}\text{-}ClCH{=}CHCl \longrightarrow LiCl + \textit{cis}\text{-}Ph_2AsCH{=}CHCl$$

$$\textit{cis}\text{-}Ph_2AsCH{=}CHCl + LiPPh_2 \longrightarrow \textit{cis}\text{-}Ph_2AsCH{=}CHPPh_2 + LiCl$$

Lithium diphenylarsenide reacts with *trans*-1,2-dichloroethylene to produce *trans*-1,2-*bis*(diphenylarsino)ethylene [54]. The same reagent also reacts with excess *cis*- or *trans*-1,2-dichloroethylene to give (2-chlorovinyl)diphenylarsine stereospecifically. The reaction between *cis*- and *trans*-(2-chlorovinyl)diphenyl arsine and Li(PPh_2) is also stereospecific and yields *cis*- or *trans*-1-diphenylarsino-2-diphenylphosphinoethylene. Sodium dimethylarsenide reacts with *cis*-(2-chlorovinyl)diphenylarsine to yield only *cis*-1-dimethylarsino-2-diphenylarsinoethylene; but with *cis*-1,2-dichloroethylene both *cis*- and *trans*-1,2-*bis*(dimethylarsinoethylene) are formed. The synthesis of 1,3-*bis*(3'-dimethylarsinopropylthio)propane, $Me_2As[CH_2]_3S[CH_2]_3S[CH_2]_3AsMe_2$ has been described [55]. The aromatic ligand, (*o*-diphenylarsinophenyl)diphenylbismuthine,*o*-$C_6H_4(AsPh_2)(BiPh_2)$ has also been prepared [56].

Abraham and Van Wazer [57], by the reaction of $RAsCl_2$ (R = C_6H_5, Me) with $P(OMe)_3$ in methylene chloride, prepared $RAs[P(O)(OCH_3)_2]_2$. The reaction of $C_6H_5AsI_2$ with $P(OCH_3)_3$ gave $C_6H_5As(I)\text{-}As(I)C_6H_5$ as a bright yellow solid, m.p. 175-177°. In a related study, the same investigators [58] prepared $C_6H_5As[P(O)(CH_3)(OCH_3)]_2$ by the reaction of one mole of $C_6H_5AsCl_2$ with excess $CH_3P(OCH_3)_2$. The same study reported the formation of tetraphenyldiarsine by the reaction between $(C_6H_5)_2AsCl$ and $CH_3P(OCH_3)_2$ or by the reaction of $(C_6H_5)_2AsCl$ with $(C_6H_5)_2AsP(O)(CH_3)OCH_3$.

Chloromethylarsonic acid is reduced by Zn/H_2SO_4 to chloromethylarsine. The ^1H NMR, mass and infrared spectra of this compound have been studied [59]. Reduction of chloromethylarsonic acid by H_3PO_2 results in the formation of *pentakis*(chloromethyl)cyclopentaarsine (PCCA) [60]. PCCA is characterized by thermal and oxidative stabilities greater than that of other cyclopolyarsines. The dynamic ^1H NMR properties of this molecule are interpreted in terms of a combination of a low-energy pseudorotational motion and a higher energy arsenic atom inversion process. Primary alkyl arsines yield the pentamers, e.g., $(CH_3As)_5$ by reaction with dibenzylmercury [61]. Dialkylarsines react with dibenzylmercury to yield both the tetraalkyldiarsine, e.g., $(CH_3)_2AsAs(CH_3)_2$ and the substitution product, $(CH_3)_2AsCH_2C_6H_5$. Methyl-dichloroarsine undergoes reaction with dibenzylmercury to give the monosubstitution product. The reaction of $(CH_3)_2$ AsI_2, on the other hand, affords a mixture of products which include CH_3As $(CH_2C_6H_5)_2$ along with $(CH_3)_2AsI$, and $(CH_3)_2AsCH_2C_6H_5$. Rheingold and co-workers [62,63] have carried out dynamic NMR studies of dimethylarsenic condensation reactions. The following equilibrium is established upon combination of $(CH_3)_2AsH$ with $(CH_3)_2AsX$ (X = halogen).

$$(CH_3)_2AsH + (CH_3)_2AsX \rightleftharpoons (CH_3)_2AsAs(CH_3)_2 + HX \qquad \text{(I)}$$

The anticipated $(C\underline{H}_3)_2AsH$ doublet is collapsed to a singlet or a very broadened doublet. This is explained in terms of an NMR-fast hydrogen exchange as shown in (II).

$$(CH_3)_2AsH + H^{*}X \rightleftharpoons (CH_3)_2AsH^{*} + HX \qquad \text{(II)}$$

For halogen systems, K for eq. I is always less than 1.0 at 30°, i.e., favoring the starting materials. However, for X = CN, K is >100 for eq. I. Furthermore, for eq. II, X = CN is too slow to cause a collapse in doublet multiplicity when excess $(CH_3)_2AsH$ is present. This is explained in terms of appreciably greater bond energy of HCN.

The interaction of HX with $(CH_3)_2AsH$ can lead to the formation of H_2. The yield of hydrogen was zero for X = CN, extremely small for X = Cl, but about 15% for X = Br, I. The formation of hydrogen is explained by eq. III-a, b.

$$\begin{array}{l}(CH_3)_2AsH + HX \overset{a}{\rightleftharpoons} [(CH_3)_2AsH\cdot HX] \\ {[(CH_3)_2AsH_2]^{+}X^{-}} \overset{b}{\rightleftharpoons} (CH_3)_2AsX + H_2\end{array} \qquad \text{(III)}$$

Eq. III-b may be reversible. As-As/As-X exchange (except for X = CN) as shown by eq. IV was also invoked in order to explain the NMR chemical shifts.

$$(CH_3)_2AsX + (CH_3)_2AsAs^*(CH_3)_2 \rightleftharpoons (CH_3)_2As^*X + (CH_3)_2AsAs(CH_3)_2 \qquad (IV)$$

Equilibrium and thermodynamic parameters were obtained [63].

Lewis and Edris [64] have measured the photoconductivity of single crystals of *cis*[catena-poly(methylarsenic)]. All samples exhibited intrinsic photoconductivity behavior for photon energies >1.55 eV. The value of the optical energy gap is in excellent agreement with the thermal energy gap determined from electrical-conduction studies. Impurity photoconduction probably arose from iodine impurities introduced by the starting compounds. Explanations are offered for the various electrical properties observed in the impurity region.

Tris(trifluoropropynyl)arsine, $As[C{\equiv}C{-}CF_3]_3$, which melts at 23-24°, has been prepared by Lemmon and Jackson [65] by the reaction between $AsCl_3$ and lithium trifluoropropynide. Detailed mass spectral data were obtained. The reactions of $Me_2AsC(N_2)H$ with metal amides have been studied by Glozbach and Lorberth [66]. The compounds prepared have the general formulas: $Me_3M(Me_2As)CN_2$ where M = Si, Ge, Sn, Pb; $Me_2M'(Me_2As)CN_2$ where M' = Sb, Bi; and $Hg[C(N_2)AsMe_2]_2$. The chemical reactivities and chemical stabilities resemble those of the *bis*-(metalorganic)diazomethanes of the heavy metals. Infrared, ^1H and ^{13}C NMR data are reported. Boche and Heidenhain have prepared all-*cis*-cyclonona-1,3,5,7-tetraenyl-dimethylarsine [67]. Rapid migration of the $(CH_3)_2As$ around the C_9-perimeter was *not* observed.

A detailed analysis of the conformation of unsaturated arsines has been carried out [68]. Conformational calculations were carried out using the CNDO/2 method for third row molecules. Relative conformational energies were calculated as a function of the CCAsC and CCCAs dihedral angles for several molecules. Photoelectron spectra of dimethylvinylarsine, dimethylphenylarsine, allyldimethylarsine, trimethylarsine, dimethylphenylarsine, and benzyldimethylarsine were prepared. It was concluded that allyldimethylarsine exists in an As-*gauche* form. Surprisingly, benzyldimethylarsine is most stable in an As-*cis* form.

Dibromoalkenes undergo nucleophilic attack by arsenides to yield acetylenes [69]. Thus, the corresponding acetylene is obtained in 46% yield from BrCH=CHBr, 53% from BrCPh=CHBr and 54% from BrCPh=CPhBr. Several $R_3As{\cdot}BH_3$ adducts have been characterized [70]. The adducts are formed by the introduction of

B_2H_6 into a benzene solution of the arsine. ^1H and ^{11}B NMR data as well as enthalpies of formation of the adducts are reported. The phosphines form thermodynamically stronger complexes than do the arsines. Wang [71] has measured rate constants for the reactions of the benzyl cation with triethylarsine.

A number of publications describe the mass spectral fragmentation patterns which are undergone by arsines. Spalding [72] has studied the mass spectral fragmentation pathways of a number of substituted triarylarsines. Jones et al., [73] have carried out a comprehensive low-resolution study of the fragmentation and the rearrangement processes of $C_6F_5As(CH_3)_2$. Mass spectral studies of metal chelates in which $Me_2As(CH_2)_{12}AsMe_2$ is the donor ligand have been published [74]. The mass spectrum of $(C_6H_5)_3As$ which is produced by chemical ionization has been reported by Kober [75].

A number of physico-chemical studies in which arsines are the subject of investigation have been reported. The ^{13}C-NMR spectra of a series of palladium and platinum complexes in which the metal is coordinated to a trialkylarsine have been measured by Balimann and Pregosin [76]. It is suggested by these investigators that the ^{13}C chemical shift of the atom bound directly to arsenic serves as a useful chemical probe. Coupling constants, $^2J(Pt,C)$ and $^3J(Pt,C)$ are presented. Wuyts et al. [77] have reported on the results of their Fourier transform ^{13}C-NMR study of triphenylarsine. Watari [78] has carried out a normal coordinate analysis of the eight isotopically labelled trimethylarsine-boranes. The study includes complete assignments for all fundamentals (except the internal torsional modes). The As-C force constant was found to have the value 3.087 mdyn/Å. Swiss workers [79] have measured the ESR spectrum of X-irradiated single crystals of the radical, $(C_6H_5)_2As\cdot$. Parameters measured include the g and ^{75}As magnetic coupling tensors, and the ^{75}As quadrupole interaction tensor.

Levinson [80] has commented on the incorrectness in the assignment of an As=As double bond to several organoarsenic compounds. A study by Russian workers [81] gives values of the vapor pressure, the heat of vaporization and the entropy of vaporization of triethylarsine.

VI. Compounds Containing Arsenic-Oxygen Bonds

The reaction between $RAsCl(NEt_2)$ and a difunctional Grignard reagent, $BrMg(CH_2)_nMgBr$ yields $[RAs(NEt_2)]_2(CH_2)_n$. The latter, on treatment with HCl gives $[RAs(OH)_2](CH_2)_n$ which is converted to the difunctional organoarsinic acid by peroxide oxidation. In this manner [82] were prepared $[RAs(O)(OH_2](CH_2)_n$ where R = octyl and n = 5-8, 10, 12.

Kauffmann and co-workers [83,84] have investigated lithiomethylarsine oxides as reagents for the synthesis of functionalized hydrocarbons. Lithiomethyl-(diphenyl)arsine oxide (*a*) undergoes reactions with alkyl halides and carbonyl compounds as shown below.

$$a + R\text{-}X \longrightarrow \underset{b}{(C_6H_5)_2As(O)\text{-}CH_2R}$$

$$a + R\text{-}C(O)\text{-}R' \xrightarrow{H_2O} \underset{c}{(C_6H_5)_2As(O)\text{-}CH_2C(OH)RR'}$$

b and *c* are reduced by $LiAlH_4$ to the arsines $(C_6H_5)_2AsCH_2R$, *d* and $(C_6H_5)_2As CH_2C(OH)RR'$, *e*. Addition of halogen followed by thermal decomposition gives the haloalkane from *d* and the haloalkene from *e*.

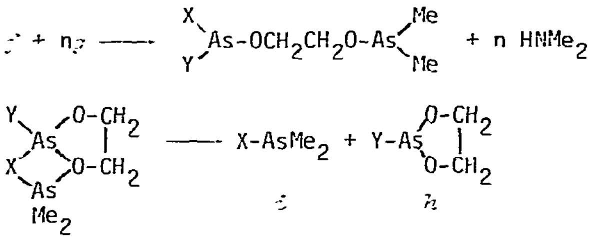
$$(C_6H_5)_2As(CH_2)_4CH_3 \xrightarrow[20\text{-}90°]{Br_2} Br(CH_2)_4\text{-}CH_3 + BrAs(C_6H_5)_2$$

$$(C_6H_5)_2AsCH_2C(OH)(C_6H_5)_2 \xrightarrow[20\text{-}120°]{Br_2} BrCH{=}C(C_6H_5)_2 + BrAs(C_6H_5)_2$$

Bromination of $(C_6H_5)_2AsCHMeEt$ to $(C_6H_5)_2AsBr_2CHMeEt$ followed by treatment with KOH or C_6H_5SNa gives EtCHMeOH and $C_6H_5SCHMeEt$, resp. $(C_6H_5)_2As(O)CMeEtLi$ reacts with $(C_6H_5)_2CO$ and H_2O to yield $(C_6H_5)_2As(O)CMeEtC(C_6H_5)_2OH$.

Alkaline hydrolysis of *tris*(*tert*-butyl)arsenate follows an S_N2 mechanism in which the OH^- nucleophile forms the five-coordinate activated complex anion, $[(RO)_3As(O)(OH)]^-$ which loses OR^- and adds OH^- in a step-wise sequence with ultimate formation of AsO_4^- [85].

Tris(dimethylamino)arsine, *f*, reacts with arsinous acid diolesters, $Me_2AsOCH_2CH_2OH$, *g*, to form arsolanes, *h*, and arsines, *i*. The reaction mechanism is that shown below [86].

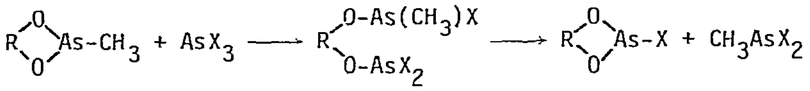


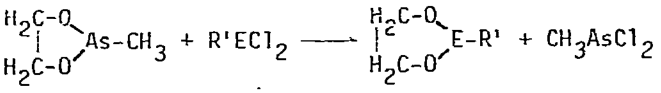
n = 1, X = Y = NMe_2

n = 2, X = NMe_2, Y = $Me_2As-OCH_2CH_2O$

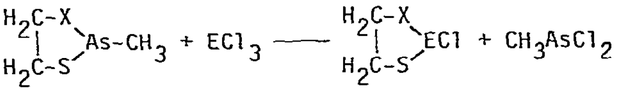
n = 3, X = Y = $Me_2As-OCH_2CH_2O$

Kober and Rühl [88] have studied the exchange reaction between cyclic arsonous acid esters and various halides. Typical reactions studied are shown below.



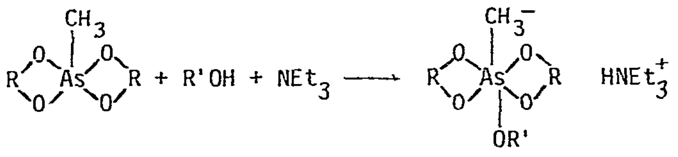


($R'ECl_2$ = PCl_3, $SOCl_2$, $(CH_3)_2SiCl_2$



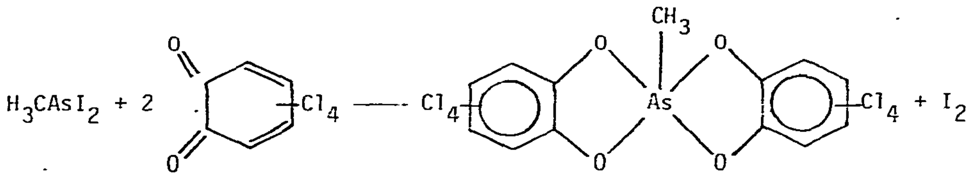
(E = P, As; X = O, S)

Wieber and Mallon [88] were able to prepare six-coordinate, water-free arsenic anions, i.e., organooximethyl*bis*(*o*-phenylenedioxo)arsenate^{-1}. This was done by the reaction of diheteroorgano-λ^5-arsols with alcohols in the presence of triethylamine.

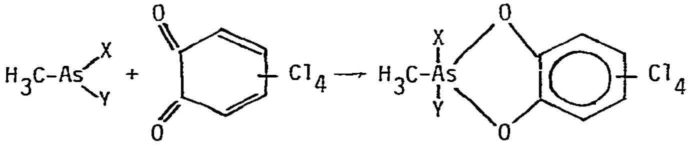


R = C_6H_4

Wieber and Götz [89] studied the oxidation of 2-iodo-1,3,2-diheteroarsolanes by *o*-chloranil. Cleavage of the As-I bond occurs with concurrent formation of spirocyclic As(V) compounds. The same oxidizing agent cleaves both AsI bonds in methyldiiodoarsines in the manner shown by the equation:



In a subsequent related publication [90] the same authors noted that several substituents other than iodine do not undergo oxidative cleavage. Instead, they are retained and the oxidation by chloranil proceeds in the manner shown below.



where X and Y may be methoxy, ethoxy, chlorine, piperdine, diethylamine, methylphenylamine, or azacyclopentane.

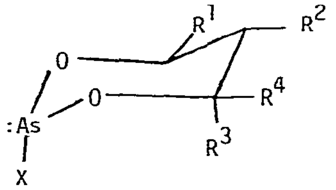
Details on the synthesis of 2-iminoxy and 2-diethylaminoxy-1,3,2-dioxaarsacyclopentanes and -cyclohexanes have been published [91]. The synthetic methods involve the reactions of 2-chloro-1,3,2-dioxaarsacyclopentanes and -cyclohexanes with oximes and diethylhydroxylamine. The physical properties of 23 of these derivatives are reported.

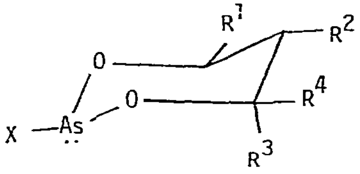
The reaction of $(C_6H_5)_3AsO$ with *n*-butyl bromide yields hydroxytriphenylarsonium bromide [92]. The reaction of $R(As)(OR')_2$ with R"X to give $R''OAs(OR')_2$ takes place *via* an S_N2 mechanism and proceeds more easily with X=I than Br [93]. The reaction of R_3AsO with $R'_2CHCHXR''$ to give $R'_2C=CHR''$ also proceeds *via* an S_N2 mechanism. Additional kinetic data on the reactions of arsines oxides with *n*-butyl iodide have been compiled [94]. In benzene-acetone solvent, treatment of

$Me_2C_6H_5AsO$ with HCl yields $[Me_2C_6H_5AsOH]Cl$. A number of alkyl- and aryldi-*o*-tolyarsines have been prepared by Sigauri and co-workers [96]. The preparative method involved the reaction between $(o\text{-}CH_3C_6H_4)_2AsOC_5H_{11}\text{-}iso$ and RMgBr. *Tris*-(triphenylmethyl)arsenite [97] has been synthesized by the reaction between *tris*-(diethylamino)arsine and triphenylcarbinol.

Studies of the vibrational spectra of five trialkyl arsenites (infrared and Raman) as a function of temperature [98] give evidence characteristic of rotational isomerism. The changes are most pronounced in the region from 550-700 cm^{-1}, especially in going from the liquid to the crystalline phase. The most stable conformations for various alkyl substituted $(RO)_3As$ compounds are suggested.

The deshielding influence of the As-O group has been demonstrated in ^1H NMR studies of about 15 arsines oxides and orthoarsenate esters [99]. Cyclic arsenites have also been the subject of ^1H NMR spectral analysis [100]. The NMR data are statisfactorily explained in terms of two chair conformations which differ with respect to the substituent on the arsenic atom. Of fifteen compounds studied, thirteen display ^1H NMR patterns which are explicable in terms of two chair conformations which differ only with respect to the *axial* or *equatorial* configuration of arsenic (see below).





In the case of two other compounds, the situation is more complex, involving conformational equilibria about the ring carbon atoms as well.

A number of physicochemical studies on As-O bonded compounds have been reported. The mass spectra of $As(OMe)_3$ and $As(OEt)_3$ were measured experimentally [101]. The experimental spectra agreed well with values calculated as functions of excitation energy using a simplified equation of quasi-equilibrium theory. A number of nuclear quadrupole resonance (NQR) spectra of ^{75}As in organoarsenic compounds containing As-O bonds have been measured. Zakirov and co-workers [102], using the ^{75}As NQR method, have investigated molecules of the following type: $(RO)_3AsO$, $RAs(O)(OR')_2$, $R_2As(O)OR'$, $(RO)_3As$ and $EtAs(OEt)_2$. In general, the higher the coordination number of arsenic, the lower is the observed ^{75}As NQR resonance frequency. The ^{75}As NQR frequencies were correlated with the sum of the Taft induction constants. In the case of alkylarsonic and dialkylarsinic acids [103] the correlation of the NQR frequencies with the total electronic effect indicates that the primary factor is that arising from the inductive effect of the substituent.

Chatterjee and Sen Gupta [104,105] have determined the crystal structure of *o*-aminophenylarsonic acid. The structure of the crystalline adduct which forms between triphenylarsine oxide and pentafluorophenol has been determined [106]. The O···O distance, 2.599Å indicates the formation of a strong hydrogen bond involving the hydroxyl group of the phenol and the arsenyl-oxygen. Crystal structures have been reported for compounds in which arsine oxides are coordinated to Ni(II) or Mg [107], U(IV) [108] and Co(II) [109].

Studies of the vibrational spectra of $(RO)_3AsO$ compounds have been carried out as a function of temperature [110]. On cooling, $\nu(As = O)$ at 980 cm^{-1}, observed in the liquid, disappears entirely in the crystal. Also, an entire new series of bands replace $\nu(AsO_3)$ in the 600-700 cm^{-1} region. The disappearance of $\nu(As = O)$ in the liquid and the appearance of $\nu(As\text{-}O\text{-}As)$ bands in the crystal is attributed to the formation of As-O-As bonded dimers. Heats of formation, dipole moments, H-bond polarities and chemical shifts of OH protons have been determined for the interaction between trichloro- and trifluoroacetic acids and *tris*(*n*-octyl)arsine oxide [111]. The phase diagrams for the systems triphenylarsine oxide-phenol (or alcohol) have been published [112]. Wauchope [113] has measured acid dissociation constants for H_3AsO_4, $pK_2 = 7.089$; for $CH_3As(O)(OH)_2$, $pK_1 = 4.114$; for $(CH_3)_2As(O)OH$, $pK_1 = 6.288$. The basicities, based on proton acceptor strengths, of 22 organoarsenic compounds of the types R_3AsO, $R_2As(O)OH$, $R_2As(O)OR'$, and $RAs(O)(OR')_2$ have been correlated with substituent constants [114]. The effects of alkyl chain length on the thermodynamics of proton ionization from arsonic and arsinic acids have been measured [115]. The changes in $\Delta G°$, $\Delta H°$ and $\Delta S°$ with increasing chain length for both arsonic and arsinic acids differ from those predicted, *e.g.*, protonated amines, protonated amino acids and carboxylic acids. A satisfactory explanation is not presently available. The thermal stability of *o*-$[(HO)_2(O)As]_2C_6H_4$ along with its ultraviolet and infrared spectra have been reported [116]. French workers [117] have investigated the dissociation of carboxymethylarsonic acid. The proton most easily dissociated is that of the hydroxyl group attached to arsenic for which $K_1 = 1.39 \times 10^{-2}$; the next proton most easily dissociated is that of the carboxyl group for which $K_2 = 1.49 \times 10^{-4}$; the trivalent ion is $^{-}OOC\text{-}CH_2AsO_3^{=}$ and $K_3 = 1.46 \times 10^{-9}$. The formation constant of $[Cr(OOCCH_2AsO_3)]$ is 4.74×10^{10}. Acid dissociation constants for a number of alkyl-, arylarsonic and dialkylarsinic acids have been measured in dimethylformamide. As expected, dialkylarsinic acids are weaker than alkylarsonic acids [118]. The compound, $HOOCCH_2As(O)(OH)_2$ for which $pK_1 = 8.95$ was the strongest acid among those studied while $(C_5H_{11})_2As(O)OH$, for which $pK = 14.65$ was the weakest. The interaction of triphenylarsine oxide with alcohols and phenols, i.e., the $\equiv As{=}O\cdots H\text{-}O\text{-}$, interaction has been studied using infrared spectroscopic techniques [119]. Infrared spectroscopy has also been utilized in the study of the adsorption of arsonic acids by natural tin dioxides and other minerals [120].

The effect of phenylarsonic acid on the sorption of zirconium and hafnium on silica-gel from acid solutions has been studied [121]. These studies have been carried out in connection with the investigation of fission-product separations. The extraction by *tris*(*n*-octyl)arsine oxide in benzene of Mo(VI) from its aqueous acid solutions was found to be very high in the pH range 3-4 [122].

Overlap integrals and the basicities of four-coordinated arsenic compounds have been discussed [123]. The basic strengths follow the order:

$$(RO)RAs(O)NR'_2 > R_3AsO > R'_2As(O)OR > (RO)_2As(O)R' > (RO)_3AsO$$

Finally, in contrast with triphenylstibine and -bismuthine, which are solvolysed in chlorosulfuric acid, triphenylarsine is oxidized to the protonated form, $(C_6H_5)_3AsOH^+$ [124].

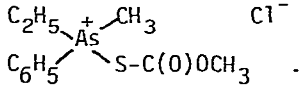
VII. Compounds Containing Arsenic-Sulfur or Arsenic-Selenium Bonds

Very little has been reported on arsenic-selenium bonded compounds. Both thio and seleno sugars form *S*- or *Se*-dimethylarsino derivatives. Chen, et al., [125] have prepared *S*- and *Se*-dimethylarsino derivatives of α-D-glucopyranose substituted at C6. The reaction of triphenylarsine with SeO_2 gives the interesting addition compound, $(C_6H_5)_3AsO \cdot SeO_2$ [126]. Triphenylarsine does not react with elemental red selenium in boiling organic solvents.

A chlorodiorganylthioarsorane has been reported for the first time [127]. Amido*bis*(*tert*-butyl)arsine reacts with elemental sulfur to form amido*bis*(*tert*-butyl)arsine sulfide. The addition of HCl in ether to the latter converts it to chloro*bis*(*tert*-butyl)arsine sulfide (I). Some reactions of I are summarized by the following scheme.

$$\mathrm{I}\quad\begin{array}{l} + \mathrm{Ph_3P} \longrightarrow \mathrm{Ph_3PS} + (t\text{-Bu})_2\mathrm{AsCl} \\ + \mathrm{RMgCl} \longrightarrow (t\text{-Bu})_2\mathrm{As(S)R} \\ + \mathrm{R_2NH} \longrightarrow (t\text{-Bu})_2\mathrm{As(S)NR_2} \\ \xrightarrow{140^\circ} t\text{-BuCl} + (t\text{-BuAsS})_x \\ + \mathrm{H_2O} \longrightarrow (t\text{-Bu})_2\mathrm{As(S)OH} \end{array}$$

The Russian school continues its activity in the field of arsine sulfides. A number of aryl- and alkylarylarsine sulfides have been prepared in the conventional manner (arsine + sulfur) and characterized [128]. A number of papers have been published which deal with reactions between arsine sulfides and halogen containing molecules. When $R_2R'AsS$ (R = Me, Et, Pr, Bu; R' = Et, Pr, Bu, Ph) undergoes reaction with $BrCCl_3$, an alkyl group is lost and $RR'AsSCCl_3$ is formed in 24-52% yield [129]. Carbon tetrachloride is inert. The reaction of ethylmethylphenylarsine sulfide with methylchloroformate gives not only the expected ethyl[(methoxycarbonyl)thio]phenylarsine, $(C_2H_5)(C_6H_5)As\text{-}S\text{-}C(O)OCH_3$, but also ethyl(methoxycarbonyl)phenylarsine sulfide, $(C_2H_5)(C_6H_5)As(S)C(O)OCH_3$ [130]. The proposed mechanism is one in which the electron pair on sulfur undergoes electrophilic attack by the carbon atom of methyl chloroformate with the formation of a *quasi*arsonium compound as an intermediate,



Isolation and identification of the *quasi*arsonium salt is offered in support of the proposed mechanism. Treatment of arsine sulfides with acetyl chloride leads to the formation of the arsine dichloride [131]. Work of a similar nature has been reported [132] in which the reactions of tertiary arsine sulfides with

$$RR'_2AsS + 2\ CH_3C(O)Cl \longrightarrow RR'_2AsCl_2$$

acetyl and benzoyl chlorides, chloromethyl methyl ether, chloroacetonitrile and ethyl chloroacetate were studied. The formation of the tertiary arsine dichloride occurred generally, but in a few cases the arsine sulfide was recovered unchanged. With hydrogen halides, tertiary arsine sulfides also yield the tertiary arsine dihalide [133].

The reaction of phenylpropyliodoarsine with (-)menthol in pyridine gives the menthyl phenylpropylarsinite

$$(C_3H_7)(C_6H_5)AsI + HO(C_{10}H_{19}) \longrightarrow (C_3H_7)(C_6H_5)AsO(C_{10}H_{19})$$

The arsinite adds a mole of sulfur to form a mixture of diastereoisomers of *O*-menthyl phenylpropylarsinothioate. By fractional crystallization from hydrocarbons, the ester can be resolved into its diastereoisomeric forms. In this way, a number of optically active tertiary arsine sulfides were prepared and resolved [134]. Asymmetric esters of alkylarylthioarsinic acids have been synthesized and their properties described [135]. The esters studied have the general formula RPhAs(S)(OR'). The ^1H NMR spectra of four triorganylarsine sulfides have been measured [136]. The ultraviolet spectra of a number of tertiary arsine sulfides have also been reported [137]. In this study the dependence of the frequency difference between the K-band maximum of di- and monosubstituted phenyl groups on K-band shift of *p*-X disubstituted benzenes is discussed. With respect to the benzene ring, the $As(S)Et_2$ group is a poorer electron acceptor than $As(O)Et_2$ with respect to the benzene ring. Differential thermal analysis (DTA) has been used as a tool to study the thermal rearrangement of tertiary arsine sulfides. The rearrangement is catalyzed by alkyl halides [138]. The mechanism of catalysis is believed to involve the intermediate formation of *quasi*arsonium salts to give esters of thioarsenous acid.

A number of alkylthioarsonium salts having the general formula $[RR'_2AsSC_2H_5]BF_4$ have been prepared and characterized [139]. The ^1H NMR spectra of a number of these and other alkylthioarsonium salts have been recorded [140].

Triorganylarsine oxides undergo an oxidation-reduction with thiols to yield the arsine and the disulfide [141]. In this particular study the reaction was carried out in dry benzene under nitrogen. A reaction takes place between diethylarsinic acid and 1,2-ethanedithiol to form 1,2-dithio*bis*(diethylarsine) ethane which disproportionates to triethylarsine and 2-ethyl-1,3,2-dithiaarsolane

Bis(dimethyldithioarsinato) complexes of VO(IV) have been prepared [142]. The formula of the compound is $OV[S_2As(CH_3)_2]_2$ and its mass and ESR spectra, magnetic susceptibility and thermal behavior were investigated. The crystal structure of $Br_2As[S_2CN(Et)_2]$ has been determined [143]. Two units are centrosymmetrically coupled to dimers with two bromide bridges between 5-coordinated arsenic centers. The As-S bond distances are 2.270 and 2.374 Å and the As-Br distances are 2.404, 2.920 and 3.066 Å. Infrared and Raman studies of the fundamental ν(As=S) vibration have been carried out [144].

VIII. Compounds Containing Arsenic-Halogen (Halogenoid) Bonds

Diaryl(phenylethynyl)arsines have been prepared in good yields by the reaction between diarylchloroarsines with the product formed by the reaction of alkylhalomagnesiums with phenylacetylene [145]:

$$C_2H_5MgBr + C_6H_5C{\equiv}CH \longrightarrow C_6H_5C{\equiv}CMgBr + C_2H_6$$

$$Ar_2AsCl + BrMgC{\equiv}C_6H_5 \longrightarrow Ar_2AsC{\equiv}CC_6H_5$$

Secondary alcohol derivatives of the type $Ar_2AsC{\equiv}CCH(OH)R$ were synthesized by the reaction between Iotsich reagents and diarylchloroarsines:

$$2\ C_2H_5MgBr + RCH(OH)C{\equiv}CH \longrightarrow RCH(OMgBr)C{\equiv}CMgBr + 2\ C_2H_6$$

$$Ar_2AsCl + BrMgC{\equiv}CCH(OMgBr)R \longrightarrow Ar_2AsC{\equiv}CH(OH)R$$

Dimethylhaloarsines react with thiourea (tu) in aprotic solvents to yield 1:1 and 1:2 addition compounds formulated as $Me_2As(tu)^+X^-$ and $Me_2As(tu)^+X^-{\cdot}tu$. The cationic nature of the trivalent arsenic is evidenced by the study of vibrational spectra which show the presence of an As-S, but absence of an As-X covalent linkage [146]. The crystal structure of $[Me_2As(tu)]^+Cl^-{\cdot}tu$ reveals that the As-Cl bond distance, 3.715 Å, is so long that the bonding is ionic. Enthalpy changes for the decomposition of the adducts to yield Me_2AsX and tu (thiourea) were measured.

The vibrational analyses for a number of haloarsines has been carried out. A normal coordinate analysis of $(CF_3)_2AsX$, where X = I, Br, Cl, F has been reported by Demuth [147]. The same group [148] has investigated the vibrational spectra of CF_3AsX_2 molecules and performed normal coordinate analyses. Vibrational spectra have also been measured for simple (C_1-C_4) alkyldichloroarsines [149]. Raman and infrared spectra of $MeAs(CN)_2$ have been recorded [150]. The $\nu(As\text{-}C_{CN})$ stretch occurs in the region 400-600 cm^{-1}. Evidence is presented for intermolecular As···N bonds.

The radicals, $[(Me_3Si)_2CH]_2As{\cdot}$ or $[(Me_3Si)_2N]_2As{\cdot}$ have been characterized by their e.s.r spectra [151]. These radicals are very persistent, $t_{1/2} > 30$ days. They are prepared by the photolysis of the corresponding arsenic chlorides in the presence of an electron-rich olefin.

Chlorine-35 nuclear quadrupole resonance spectroscopy has been used as an investigative tool for the study of a number of As-Cl bonded compounds. Jugie et al., [152] have measured the ^{35}Cl NQR resonances of the series of molecules R_nAsCl_{3-n} and $(RO)_nAsCl_{3-n}$. The directions of the shifts, which increase with an increase in the number of Cl atoms and decrease as the number of alkoxy group increases, is interpreted in terms of the electronegativity of Cl, which decreases the electron density on As and a back-donation of electrons from the oxygen on the alkoxy group to the arsenic atom. From a ^{35}Cl n.q.r. study [153] it is indicated that $AsPhCl_4$, $AsPh_2Cl_3$ and $AsPh_3Cl_2$ all possess trigonal-bipyramidal structures in the solid state with the phenyl groups occupying equatorial positions. In Me_3AsCl_2 and Me_2AsCl_3 the methyl groups occupy equatorial sites in trigonal-bipyramidal structures. Adducts of As(V) compounds with Lewis acids, X, such as BCl_3, $SbCl_5$, or ICl have the expected ionic structures, $[AsR_nCl_{4-n}][XCl]$.

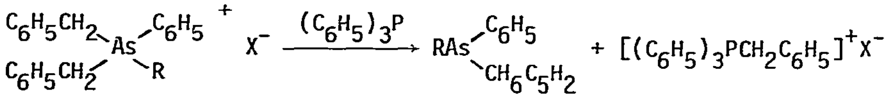
The mass spectral fragmentation patterns of AsX_3, X=I, Br, Cl, F, obtained by chemical ionization have been compared with those obtained by electron impact [154]. The mass spectral fragmentation of methyldihaloarsines has also been investigated [155]. The formation of halogen bridged dimers which lose halogen atoms, but not methyl groups, is observed.

The He I photoelectron spectra of a number of $MeAsX_2$ and Me_2AsX compounds have been interpreted [156] in terms of a "composite molecule" approach derived for C_{3v}/C_5 systems. Since analogues containing the other group V elements, N, P, Sb were also measured, a trend comparison was made. Ionization energies were assigned.

IX. Triorganyl Arsines

A. Asymmetric Triorganylarsines

Two closely related papers [157,158] describe the resolution of aminophenylethyl-*m*-tolylarsines into the optically active isomers (*o*-,*m*-,*p*-aminophenyl). The procedure involves the preparation of the diastereomeric (+)-tartrates and fractional recrystallization from ethanol. The alkylation of phosphines by arsonium salts has been utilized for the synthesis of asymmetric arsines [159]. The reaction proceeds as follows and it is preferably carried out in an aprotic solvent such as dimethylformamide.



$$[(C_6H_5CH_2)_2As(C_6H_5)R]^+X^- \xrightarrow{(C_6H_5)_3P} RAs(C_6H_5)(CH_6C_5H_2) + [(C_6H_5)_3PCH_2C_6H_5]^+X^-$$

The reaction proceeds best when X = I. The benzyl group is preferentially eliminated from the arsonium salt. Another route for the synthesis of asymmetric tertiary arsines [160] utilizes the ability of aryloxoarsines to react with Grignard reagents. The pertinent reactions are as follows:

$$(ArAs{=}O)_n + nRMgX \longrightarrow nRArAsOMgX$$

$$RArAsOMgX + HX \longrightarrow RArAsX + Mg(OH)X$$

$$RArAsOMgX + R'MgX \longrightarrow RArAsR' + MgX_2 + MgO$$

Benzylisopropylmethylphenylarsonium bromide has been synthesized and separated into its enantiomers [161]. The absolute configuration of the dextrorotatory stereoisomer has been established primarily through the use of fusion diagrams.

B. Other Aspects of Triorganylarsines

In an investigation designed to produce more powerful nucleophilic reagents, Lorberth and co-workers [162,163] have prepared a number of organometallic diazoalkanes including the following arsenic derivatives: $(Me_2As)_2CN_2$, $Me_2AsC(N_2)COOEt$, $Me_2As[C(N_2)COOEt]_2$, $MeAs(NMe_2)C(N_2)COOEt$, and $(Me_2N)_2AsC(N_2)COOEt$. Enhanced nucleophilic properties are revealed by ^{13}C NMR shifts. In the series of compounds just referred to the $\delta As{-}^{13}CH_3$ shift is 9.9, 9.3, 6.8 and 9.7 ppm, resp.; $\delta M{-}^{13}C(N_2)$ shifts are 24.7, 45.7, 27.2, 46.4 and 38.4, resp. Compounds of the type $L_nMC(N_2)R$ undergo 1,3-dipolar cycloaddition reactions to $MeO_2C{\equiv}CCCOOMe$ when M = Sn, Pb, Sb, Bi or Hg and L = Me. When M = As, no reaction is observed and this is attributed to steric effects.

Secondary arsinocarboxylic acid derivatives have been synthesized [164] by the reaction between alkali metal salts of alkylarsines, MHAsR and halocarboxylic acids in liquid ammonia as follows:

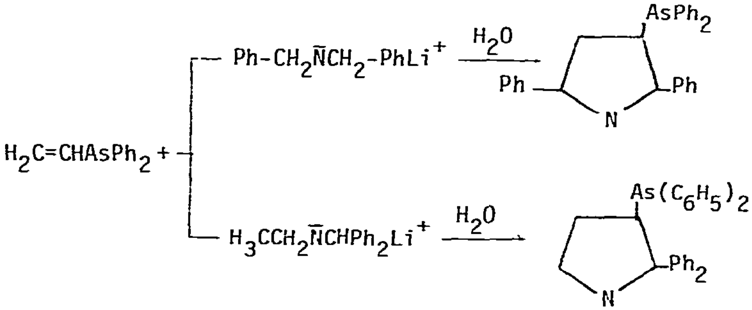
$$MAs(H)R + X{-}R'{-}COOY \longrightarrow RAs(H){-}R'{-}COOY + MX$$

R = n-Bu, C_6H_5; R' = $(CH_2)_n$, CHMe, CHEt; X = Cl, Br; M = Na, K;
Y = OM, OR', NH_2; n = 1-4, 10.

Reactions of these compounds include substitution at Y, conversion to the carboxylic anhydride and its conversion to the amide, and reduction of COOR' to the alcohol.

Peterson and Pizey have prepared and studied a number of α-styrylarsines [165]. The compounds are formed by the reaction between $AsCl_3$ and phenylacetylenes. The As-Cl bonds in the compounds are exceedingly sensitive to hydrolysis The As-Cl bonds undergo reaction readily with C_6H_5MgBr to yield the diphenylarsino derivative. The vinylic chlorine can be reduced by $LiAlH_4/LiH$ to give the styrylarsine.

The cycloaddition of 1,3-diphenyl-2-azallyllithium and 1,1-diphenyl-2-azallyllithium across the double bond of diphenylvinylarsine has been studied by Kauffmann and co-workers [166]. The reaction proceeds in the manner shown by the equation



The reaction of diphenylvinylarsine with an alkyllithium in THF [167] results in a lengthening of the vinyl group

$$H_2C{=}CHAsPh_2 + RLi \xrightarrow{H_2O} RCH_2CH_2AsPh_2$$

$$R = Et,\ Bu,\ \textit{sec}\text{-}Bu,\ \textit{tert}\text{-}Bu$$

2-Aminoethylarsines or *o*-aminophenylarsines add to phenylacetylene to give mixtures of *cis*- and *trans*-styrylarsines [168]. The addition to isopropenylacetylene

$$R_1R_2AsH + HC{\equiv}CPh \longrightarrow R_1R_2AsCH{=}CHPh$$

$$R_1 = n\text{-}Bu,\ Ph,\ Et$$

$$R_2 = -CH_2CH_2NH_2,\ -CH_2CH_2NHEt,\ o\text{-}C_6H_4NH_2$$

gives 90% *trans*-4,3 and 10% of the 4,1 addition product. In the presence of pyridine, $R_2AsC{\equiv}CCH_2(OH)R'$ reacts with acetyl chloride or chlorotriethylsilane to eliminate HCl and form $R_2AsC{\equiv}CCH_2(OG)R'$, where G is $CH_3C(O)$ or Et_3Si, resp. [169].

Tris(pentafluorophenyl)arsenic reacts with *bis*(trifluoromethyl)nitroxyl to yield the adduct, *tris*(pentafluorophenyl)arsenic*bis*[di(trifluoromethyl)nitroxide] [170]. Although the antimony analogue also forms an addition compound, the phosphorus analogue is oxidized to the phosphine oxide by nitroxyl.

An interesting ligand shift involving benzyl ligands has been observed [171]. Tertiary arsines which contain benzyl ligand(s) react with 1,2-dihaloethane (halogen = I or Br) to yield the quarternary arsonium salt containing two benzyl groups as the main or sole product. The predicted formation of the *bis*(arsonium) salt either does not occur or to a very limited extent. The reaction proceeds in a manner which involves the initial formation of the tertiary arsine dihalide. The latter decomposes into the benzyl halide and the haloarsine. The benzyl halide then reacts with the original (benzyl-substituted)arsine to give the quarternary arsonium salt which bears an additional benzyl ligand. In a similar manner, diphenylethoxyarsine reacts with bromine to yield ethyl bromide and the ester of diphenylarsinic acid. The reaction of *tris*(*o*-dimethylarsinophenyl)bismuthine with sodium tetrachloropalladate(II) results in Bi-C bond cleavage, the deposition of free bismuth, and the formation of the Pd(II) complex of phenyldimethylarsine [172].

Rate and equilibrium constants have been measured for the reaction between triarylarsines and benzyl bromide in chloroform [173]. The considerably greater reactivity of the *o*-anisyl- *vs.* the phenyl compound is attributed to steric effects and to the fact that increasing electron demand (of the ether groups) results in increasing electron supply when an anchimeric assistance effect is operative (as is the case here).

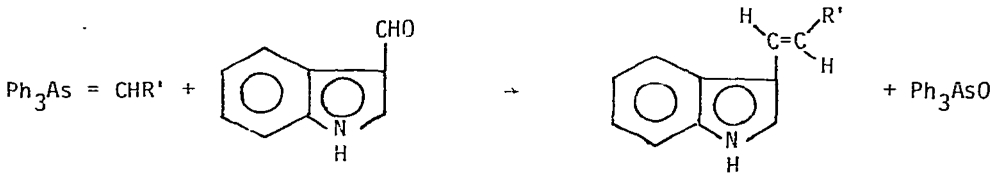
Raman and infrared spectra have been recorded for trimethylarsine [174] and its torsional barriers have been obtained. Triorganostannylarsines, $R_3SnAsPh_2$, have been shown to be configurationally stable within the NMR time scale [175]. ^1H NMR studies were carried out for a number of arylarsines over the temperature range -196° to 20°. From these data the magnetic relaxation of protons and internal rotations of arsine substituents were interpreted. No relaxations were observed which could be associated with the mobility of the phenyl ring attached to arsenic or of the methyl group linked directly to phenyl. ^{13}C NMR studies have been reported for a number of Pd^{+2} complexes in which triorganylarsines are coordinated to the metal [177]. Electron spin resonance studies [178] reveal that the exposure of solutions of Ph_3As in sulfuric acid at 77°K to ^{60}Co γ-rays yields the cation, $Ph_3As^{\dot{+}}$. In sulfuric acid, Ph_3AsO gives $Ph_3As^{\dot{+}}$, but in methanol either Ph_3AsO^- or $Ph_3\dot{A}sOR$ was formed. The quantum yield of radicals formed by the ultraviolet photolysis of Ph_3As solutions in isopropanol has been investigated [179]. The electrolytic reduction of arsinobenzoates has been found to involve a three-step process [180]. The first involves one electron and is reversible. The transfer of the second electron leads to As-C bond rupture and to the formation of benzoate esters (from alkyl substituent on the arsine). The radical anions formed during the reduction processes were studied by ESR and the quadrupole moment of As was found to make an appreciable contribution to the width of the ESR lines.

Dipole moments have been measured for a number of arsines [181,182]. The experimental moments have been discussed as a consistent set of data that allow for calculation using the vectorial additive method, of suitable group moments, bond moments and configurational parameters. The greater dipole moment of triphenylarsine, compared to that of trimesitylarsine has been attributed to the greater CAsC bond angle in the latter compound.

The crystal structure of triphenylarsine-trisulfur tetranitride has been determined [183].

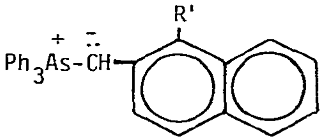
X. Arsonium Compounds, Arsenic Ylides and Arsanes

Tewari and co-workers continue their activity in the field of arsonium ylides. *Trans*-1-aryl-2-(3-indolyl)ethylenes have been prepared in good yields [184] by the interaction of arsonium ylides with indole-3-carboxaldehyde. The olefins formed have the *trans*-geometry. A new series of arsonium ylides (A),



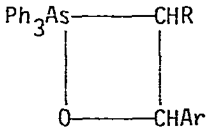
R' = nitrophenyl or bromonaphthyl

2-naphthylmethylenetriphenylarsenane, and their reactions toward carbonyl compounds have been investigated [185].



A

The reaction of A with an aryl aldehyde gives the epoxide and triphenylarsine if R' = H, but when R' = Br, the product is the olefin and triphenylarsine oxide. In both cases, the carbonyl group of the aldehyde is attached by the carbanionic center of either ylide to form a cyclic transitional intermediate (B).



B

The intermediates decompose by different paths to give the respective products. In a related study [186], semistabilized arsonium ylides were found to react with anthrone and 2-chloroanthrone at the reflux temperature of benzene to yield exocyclic olefins, obtained almost exclusively in the form of the *trans*-isomers. With 9-anthraldehyde, $Ph_3As=CHAr$ gave the *trans*-1-aryl-2-(9-anthryl)-ethylenes, exclusively. Allen and Jackson [187] have discovered that the behavior of arsonium betaines contrasts with that of the phosphonium analogues. They investigated steric effects, by enclosure of the arsenic in the strained dibenzarsolium ring system and electronic effects, by the presence of the electron-withdrawing 2-furyl substituent on the arsenic. In neither case was betaine collapse *via* attack of betaine oxygen at the arsonium center observed.

Both 2-furyl(methyl)diphenylarsonium iodide and 5-methyl-5-phenyldibenzylarsoniu iodide, on treatment with benzaldehyde and NaOEt gave the olefin epoxide and and tertiary arsine, exclusively. Gosney, Lillie and Lloyd [188] studied product formation, i.e., epoxide + arsine *vs.* olefin + arsine oxide as a function of the substituents on arsenic. The olefin/epoxide product ratio was found to increase as the electron donating ability of the organic substituent on arsenic increased.

Triethylmethylenearsorane has been prepared by the dehydrohalogenation of triethylmethylarsonium salts by $NaNH_2$ [189],

$$[(C_2H_5)_3\overset{+}{As}CH_3]\overset{-}{Br} \xrightarrow[-NaBr]{NaNH_2} (C_2H_5)_3As=CH_2.$$

The same compound can also be prepared by desilylation of triethyl(trimethylsilylmethyl)arsonium chloride (<u>C</u>)

$$Et_3As + ClCH_2SiMe_3 \longrightarrow \underset{\underline{C}}{[Et_3\overset{+}{As}CH_2SiMe_3]Cl^-}$$

$$\underline{C} \xrightarrow{BuLi} \underset{\underline{D}}{(C_2H_5)_3As=CH-Si(CH_3)_3}$$

$$\underline{D} \xrightarrow[-(CH_3)_3SiOCH]{+CH_3OH} (C_2H_5)_3As=CH_2.$$

Triethyliminoarsorane (<u>E</u>) is formed exclusively from Me_4As^+ salts and $NaNH_2$,

$$Me_4As^+Br^- \xrightarrow[-CH_4]{NaNH_2} (CH_3)_3As=NH.$$

Triphenylmethylenearsorane forms stable silver and copper complexes,

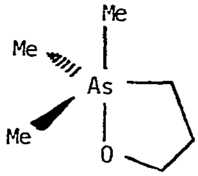
$$Ph_3As=CH_2 \xrightarrow[M=Ag,Cu]{MCl} \begin{array}{l}[Ph_3AsCH_2AgCl]_n \\ [Ph_3AsCH_2-Cu-CH_2AsPh_3]Cl\end{array}$$

The preparation of ylides of the type $Me_3As=CH-GeMe_3$ and $Me_3As=C[Ge(CH_3)_3]_2$ has been carried out as shown by the following equations [190].

$$Me_3As = CHSiMe_3 + Me_3SiOGeMe_3 \longrightarrow Me_3SiOSiMe_3 + \underset{\underline{F}}{Me_3As = CH - GeMe_3}$$

$$2\,\underline{F} \longrightarrow Me_3As = CH_2 + Me_3As = C[Ge(CH_3)_3]_2$$

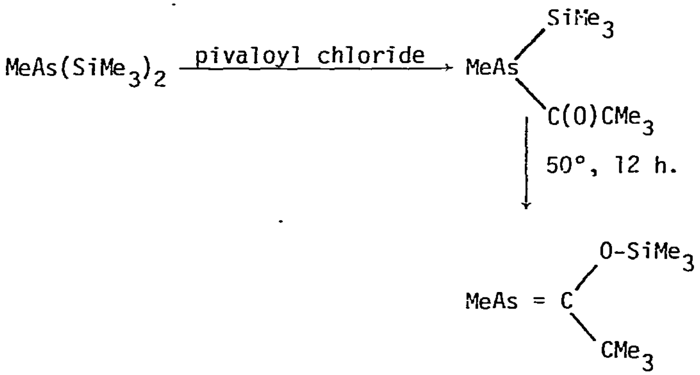
Trimethylmethylene arsorane reacts with ethylene oxide to give the 1,2λ^5-arsolane (G). From variable temperature ^1H and ^{13}C NMR data this compound has been assigned a trigonal-bipyramidal structure with a methyl group and an oxygen in axial positions [191].



G

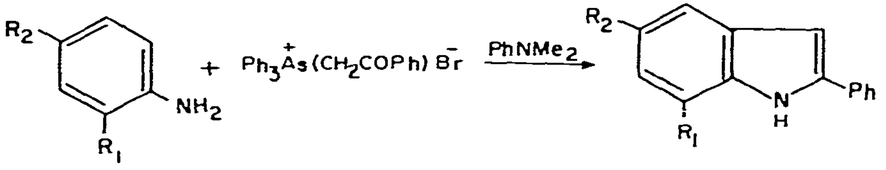
Tetraphenylarsenic reacts readily with phenyldiazonium tetrafluoroborate to form azobenzene and tetraphenylarsonium tetrafluoroborate [192].

A most interesting paper by Becker and Gutekunst [193] claims the preparation of a trivalent arsenic compound containing a formal arsenic-carbon double bond. The reaction sequence is shown as follows:



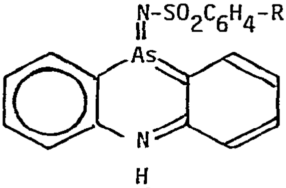
The evidence is based largely on ^{13}C and ^1H NMR spectral shifts and some infrared data. This interesting work merits further investigation and corroboration.

The synthesis of 2-phenylindoles by the reaction of phenylacyltriphenylarsonium bromide with anilines has been reported by Bansal and Sharma [194].



Yields obtained in this reaction vary from 51-72%. The cleavage of allylarsonium salts by sodium hydroxide has been studied by Samaan [195]. In general, quarternary allylarsonium salts yield tertiary arsines and allyl alcohol when treated with 0.5 M sodium hydroxide at 70-100°. However, under similar conditions, benzyltriphenylarsonium salts yield toluene and triphenylarsine oxide. At room temperature, the reaction of p-nitrobenzyltriphenylarsonium bromide with NaOH yields Ph_3AsO, Ph_3As, p-nitrotoluene and 4,4'-dinitrodibenzyl. In order to account for the formation of the last product, a mechanism involving an ylid intermediate is proposed. Ellis [196] has studied the reaction between tetraphenylarsonium salts and various cyclopentadienylmetal carbonyls. With $C_5H_5Fe(CO)_2^-$ the addition of a phenyl group gives $C_5H_5Fe(CO)_2Ph$. $Re(CO)_5^-$ reacts much more slowly and gives only $Re_2(CO)_{10}$. Less nucleophilic carbonyl anions such as $Mn(CO)_5^-$, $Co(CO)_4^-$ and $V(CO)_6^-$ give quaternary arsonium salts.

A number of optically active arsonium salts, RR'EtPhAsX have been prepared [197]. Trialkylcarbamoylmethylarsonium iodides react with CdI_2 to give tetraiodocadmates, $[R_3AsCH_2C(O)NH_2]_2CdI_4$ [198]. Phenarsazine chloride reacts with chloramines to give arsinimines (H) [199]. These compounds are active against *Sarcina lutea* and *Staphylococcus epidermis*.



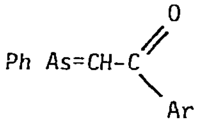
H

A Japanese patent [200] describes the use of $Ph_4As^+Br^-$ as a catalyst in the manufacture of organic isocyanates.

Tetraphenylarsonium salts of the TCNQ anion radical have been the subject of a number of physical measurements. Iida [201,202] has studied phase transitions, prepared a phase diagram and measured the thermodynamic properties of Ph_3AsMe^+-$TCNQ^{\cdot -}$ systems. Devreux and Nechtschein [203] have investigated nuclear relaxation in exciton dynamics of $[Ph_3AsCH_3][TCNQ]_2$. Using the polarizing microscope, Helberg [204] has measured the indicatrix and directions of absorption in $Me_4As \cdot [TCNQ]_2$.

Infrared, Raman and NMR analysis of R_3AsX_2 *molecules [205] lead to the* conclusion that when the X = F or Cl, such molecules possess trigonal, bipyramidal structures with idealized C_{3v} symmetry. When X = I or Br, the molecules possess tetragonal ionic structures, $[R_3AsX]^+X^-$. The crystal structure of $[(CH_3)_4As][(CH_3)_2InBr_2]$ has been determined [206].

Nuclear magnetic resonance has been used in a variety of ways in the study of arsonium salts and arsenic ylides. ^{13}C chemical shift assignments for a series of arsenic ylides have been presented by Froyen and Morris [207]. They concentrated on a series of ylides bearing a p-substituted phenacyl group linked to the carbanion (I).



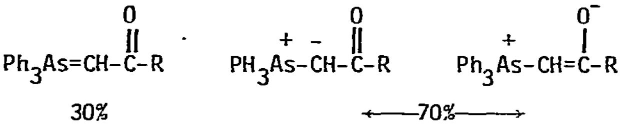
$Ph\ As{=}CH{-}C({=}O)Ar$

I

Chemical shifts of the ylide carbon in this group of molecules show a linear dependence with the dual substituent parameters of Swain and Lupton, with the resonance term predominating. The chemical shifts of the carbonyl carbon do not display such a correlation. A limited interaction between the aromatic rings attached to arsenic and the arsenic atom is indicated by the chemical shifts of those carbon atoms. ^{19}F NMR spectral studies on $(C_6H_5)_2AsF_3$ have been published [208]. In contrast with the phosphorus analogue, the arsenic compound exhibits rapid ligand exchange down to -90°. Whether this results from a Berry pseudorotation with the larger arsenic atom providing a lower energy barrier, or an intermolecular exchange process is not certain. A ^1H NMR investigation of methyl group reorientation and cation tumbling in polycrystalline $AsMe_4I$ has been reported by Rager and Weiss [209]. It is concluded that the reorientational motion of the methyl groups at low temperatures and the reorientation of the whole cation at high temperatures are responsible for the relaxation mechanism. ^1H NMR spectra of a number of arsenic(V) derivatives including ethylphenylarsonium chlorides, fluoborates and iodides have also been reported [210].

Balimann and Pregasin [211] have studied ^{75}As NMR shifts in a number of arsenic compounds including AsR_4^+ salts, AsO_4^{-3} and AsF_6^-. The latter served as a reference ion. The observed chemical shift range exceeds 600 ppm although the range for alkylarsonium salts is 50 ppm. Relative to AsF_6^-, downfield shifts from 206 ($AsMe_4^+$) to 258 ppm ($AsPr_3Et^+$) are observed for arsonium salts. The arsenate ion, $AsO_4{}^{-3}$, exhibits a downfield shift of 369 ppm relative to AsF_6^-. An upfield shift of -291 ppm is observed for AsH_4^+ as the $Ta_2F_{11}^-$ salt. Although ^{75}As chemical shifts are not strongly solvent dependent, the linewidths vary greatly in different solvents. This has been attributed to ion-pairing.

He(I) photoelectron spectra of $(CH_3)As{=}CH_2$, $(CH_3)_3As{=}CHSi(CH_3)_3$ and $(CH_3)_3As{=}C[Si(CH_3)_3]_2$ have been studied [212]. A consistent model of the electronic structure has been obtained from semiempirical MO calculations (CNDO, EHMO) and ^{13}C data. The ionization potentials and calculated total energies point to possible changes in the ylidic methyl anion upon substitution of arsenic for phosphorus. An ESCA study of the As-C ylide bond in carbonyl-stabilized triphenylarsonium ylides has been undertaken by Dale [213]. The results are consistent with the following resonance structures:

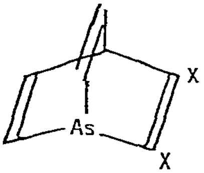


$$Ph_3As{=}CH{-}\overset{\overset{O}{\|}}{C}{-}R \qquad PH_3\overset{+}{As}{-}\overset{-}{CH}{-}\overset{\overset{O}{\|}}{C}{-}R \qquad Ph_3\overset{+}{As}{-}CH{=}\overset{\overset{O^-}{|}}{C}{-}R$$

Jananese workers [124] have measured the viscosities of aqueous solutions of arsonium halides.

XI. Arsenic Heterocycles

Ashe and Friedman [215] have prepared Diels-Alder adducts between arsabenzene and dimethylacetylene dicarboxylate. The reaction between these two reagents at 80° gives a good yield of arsabarrelene.

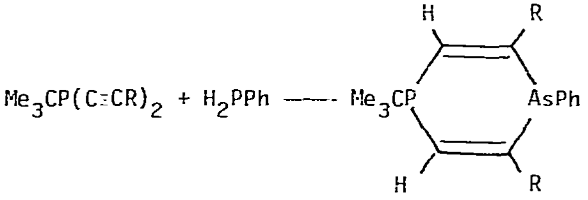


arsabarrelene

$X = CO_2CH_3$

The pyrolysis of the adduct results in an 80% yield of 2,3-dicarbomethoxyarsabenzene (A) by loss of acetylene. The same reaction sequence with 2-methylarsabenzene yields 47% of A *via* loss of methylacetylene and 43% of 6-methyl-2,3-dicarbomethoxyarsabenzene *via* loss of acetylene. In a similar manner, flash pyrolysis of the Diels-Alder adduct formed between methylpropiolate and arsabenzene gave 3-carbomethoxyarsabenzene and 2-carbomethoxyarsabenzene in a 3:2 ratio. The same authors report [216] that methyllithium adds to arsabenzene to give the 1-methyl-heterocyclohexadienide anion. The synthesis of 1,1-dimethyl-λ^5-phosphabenzene is accomplished by quaternization of 1-methyl-2,4-arsacyclohexadiene. Treatment of the arsonium salt with dimsyl ion in DMSO gives 1,1-dimethyl-λ^5-arsabenzene [217].

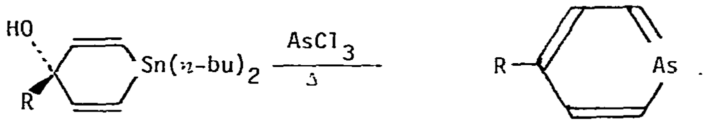
A number of papers have appeared based on the work of Märkl and co-workers. The pK of arsabenzene-4-carboxylic acid is 4.10. This value is compared with that of related compounds along with other physical measurements such as ultraviolet, ^{1}H NMR, and mass spectra [218]. The cycloaddition of phenylarsine to *bis*(propynyl)*tert*-butylphosphine gives 1,4-dihydro-1-phospha-4-arsabenzene derivatives with the isomer distribution shown below [219].



cis - 60%

trans - 40%

Atmospheric oxidation converts the phosphorus to phosphoryl. The synthesis of 4-hydroxy-1,4-dihydrostannabenzene has been described [220]. This compound reacts with $AsCl_3$ to give an oxa-arsascyclopentene which can undergo thermal rearrangement, presumably *via* a free-radical mechanism to the 4-substituted-arsabenzene.



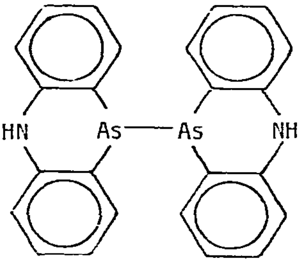
When 4-hydroxyarsabenzene is treated with an alkyl iodide in acetone solution in the presence of anhydrous K_2CO_3, the product formed is the 1-alkyl-1-arsa-cyclohexa-2,5-diene-4-one [221]. Only traces of the 4-alkoxy derivative are noted. In acid solution, 1-aryl-4-methoxy-arsacyclohexadiene loses a mole of alcohol and rearranges to 2-arylarsabenzene [222]. The rearrangement probably involves the formation of a 1-arylarsabenzene-onium intermediate in which migration of the As-aryl group to the 2-position is followed by the loss of a proton from that position to yield the 2-aryl-substituted product.

Halogen complexes which form with 1-methylarsenane have been studied by Lambert and Sun [223]. The 1:1 Cl_2 and Br_2 complexes have trigonal bipyramidal structures while the 1:2(Br_2) adduct has the "molecular complex"structure, i.e., $R_2AsMeX^+ X_3^-$, where R_2AsMe represents the methylarsenane group.

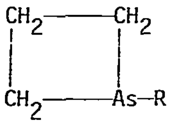
The acetylation of methyl-10-phenoxarsine by acetyl chloride in the presence of $AlCl_3$ gives the 2-acetyl and 2,8-diacetyl derivatives [224].

Because alkyl-10-phenoxarsine oxides tenaciously hold on to water, a number of derivatives were isolated and identified in the form of the anhydrous adducts formed with mineral acids, *viz.*, HCl, HBr and $HClO_4$ [225].

Dutch workers [226] have reinvestigated the structure of "phenarsazine." From chemical and spectral evidence they conclude that the aromatic, anthracene-like structure originally proposed is incorrect and that the compound actually obtained is 10,10'-*bis*(5,10-dihydrophenarsazinyl).

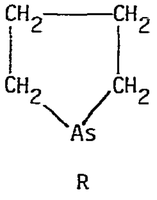


Four-membered alicyclic tertiary arsines have been prepared [227]. Treatment of 3-chloropropyl(methyl)iodoarsine and 3-chloropropyl(phenyl)iodoarsine with sodium in tetrahydrofuran yield 1-substituted arsetans. In a similar manner, five-membered homologues, 1-substituted arsolans, are prepared from 4-chlorobutylorganylarsines.



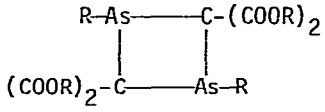
R = Ph, Me

arsetan



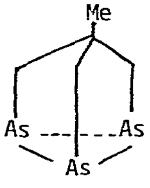
arsolan

A similar ring system, diarsacyclobutane, has been prepared by the reaction between the diester of malonic acid and alkyldichloroarsines [228]. A tertiary amine is present as a hydrogen chloride scavenger.



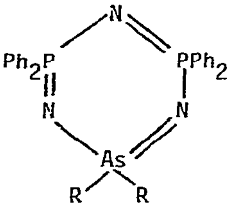
diarsacyclobutane

A number of novel arsenic-containing ring systems have been introduced. Ellermann and Schoessner [229] have utilized organotriarsines of type B in the synthesis of some metal carbonyl derivatives. 5,10-Dihydro-5,10-dimethyloctafluoroarsanthrene



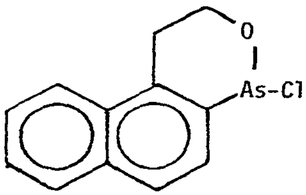
B

has been prepared [230] by the reaction between 1,2-dilithiotetrafluorobenzene and diiodomethylarsine. Sorverby and Tillott [231] have reported a mixed As-P-N heterocycle, 1,3,5,2λ^5,6λ^6,4λ^5-triaza-arsatriphosphorine, C. The reaction used involves ring closure, by arsenic(V) of linear phosphazene.

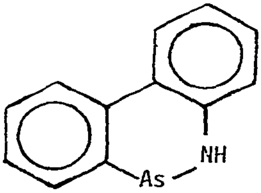


C

Bhatia and Jit [232,233] have reported the preparation of 4-chloro-1,2,3,4-tetrahydronaphth [2,1,c] [1,2] oxarsenin (D) and 6-chloro-5,6-dihydrodibenz [c,e] [1,2] azarsenine (E). System D was synthesized from 1-naphthylacetic acid by reduction with $LiAlH_4$ to the alcohol which, on treatment with $AsCl_3$ gives an intermediate dichloride. The latter, on distillation, cyclizes to D. System E is prepared by the reaction of $AsCl_3$ with 2-aminobiphenyl followed by cyclization with anhydrous aluminum chloride.

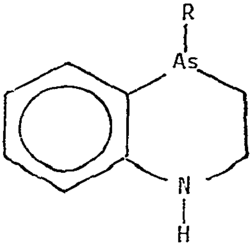


D



E

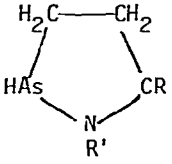
Aminoarsines of the type $As_4(NMe)_5NR$, in which R = Me and having the adamantane structure have been previously described. Kober [234] has now described the preparation of several such derivatives in which R ≠ Me. Arsatriptycene has been synthesized in a novel manner [235]. The new synthesis involves cyclization of 9-(*o*-chlorophenyl)-9,10-dihydro-9-arsanthracene with *bis*(isopropyl) N^-Li^+in THF. As-metallated *o*-aminophenylarsines react with α-halocarboxylic acids to give α-(*o*-aminophenylarsino)-carboxylic acids which cyclize to tetrahydro-1,4-benzazarsenine-2-one (F) [236].



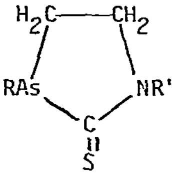
F

When 1,2-diiodotetrafluorobenzene and arsenic are heated together in an evacuated, sealed tube at 300° for three days, dodecafluoro-13,14-diarsatriptycene is obtained [237].

2-Aminoethylarsines undergo cyclocondensation reactions with aldehydes and ketones to yield 3 H-1,3-azarsolidines (G) [238] and with carbon disulfide to yield 1,3-azarsolidine-2-thiones (H) [239]. Iminoester hydrochlorides react with 2-aminoalkylarsines with formation of 1,3-azarsolines (I) [240].

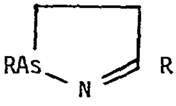


G



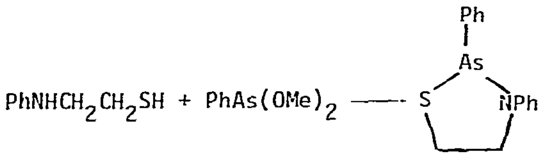
H

$$H_2NCH_2CH_2AsHR + R'C(OR'') = NH \cdot HCl \longrightarrow$$

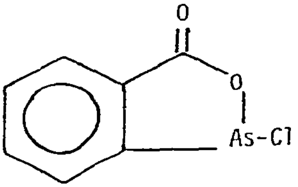


I

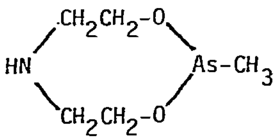
In a manner similar to that just described, but using thiolethanolamines, heterocyclic systems having an S-As-N heteroatom distribution have been prepared in the manner shown below [241]:



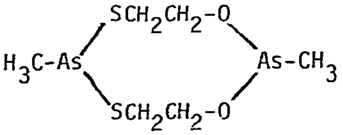
Refluxing of o-HO(O)CC$_6$H$_4$AsCl$_2$ from toluene gives the heterocyclic system J, [24]. Kober and Rühl [243] have investigated the reactions of alcoholamines and thioglycols w aminoarsines and synthesized a number of macrocyclic esters typified by K and L having 8-10 membered ring systems.



J

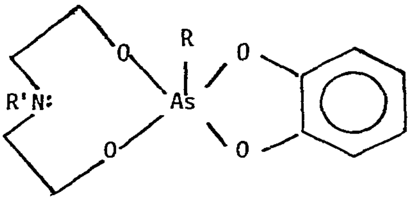


K

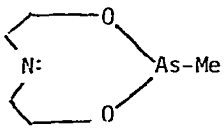


L

Maroni and co-workers [244,245,246] have also prepared 8-membered heterocylic ring systems of the types shown by M and N.



M



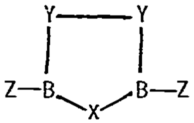
N

The crystal structure of M [244] shows octahedral coordination about arsenic with the four oxygen atoms forming the square plane of the octahedron and N and R axially oriented with respect to As. In N [245], the structure about As is trigonal bipyramidal with the two oxygen atoms and the free electron pair occupying equatorial positions and N and Me apical positions. These papers include considerable information obtained from dynamic NMR studies. Märkl and Hauptmann [247] have investigated the radical cycloaddition of phenylarsine and trimethylsilyl arsines to pentadiyn-1,4-ones-3. This reaction yields 2-methylene-arsolene-4-ones-3 which react with diphenylketene to give disubstituted 2,3-*bis* (methylene)arsolenes-4 which undergo thermal electrocyclic reactions. The resulting benzannelated arsolenes can be dehydrogenated to arsoles which can be isolated directly from the reaction of phenylarsine with 3-diphenylmethylene-pentadienes-1,4.

A considerable number of physico-chemical studies which deal with heterocyclic arsenic compounds have appeared. Using ^{1}H and ^{13}C NMR spectroscopy, Samaan [248] has determined the conformation and configuration of 1,4-ox- and -azarsenanium salts. The proton NMR spectrum of 2-dimethylamino-3-methyl 1,3,2-oxazaarsolane is very sensitive to solvent effects and temperature [249]. The spectrum was carefully analyzed and at -48° in perdeuterotoluene the molecule exists in a preferred conformation in the C4-C5 region. In nitrobenzene at 31° the spectrum corresponds to that of an A_2X_2 system which indicates free rotation about that bond. At higher temperatures a new coalescence phenomenon is explained in terms of inversion by the arsenic atom. Aksnes and co-workers [250,251] have carried out proton NMR analyses of several five-membered heterocyclic arsenic compounds. A complete analysis of 2-chloro-5-methyl- and 2-phenyl-5-methyl-1,3,2-oxathiarsolane and 2-chloro-5-methyl-1,3,2-dithiarsolane and 1,3,2-dioxarsolane was performed. Geometrical isomers were identified in solution and approximate values for the ring torsional angles were obtained. The presence of the sulfur atom tends to increase ring-puckering. The NMR data are adequately described on the basis of flexible twist-envelope conformations. A similar analysis has been carried out for ten arsolanes. A conformation analysis of 1-methylarsenane has been reported [25]. The barrier to ring reversal is 7.8 kcal. mol^{-1}. The coalescence temperature is -218° and the free energy of activation is 6.8 kcal. mol^{-1}. At -140°, the axial and equatorial conformatio are about equally populated. The R value of 2.7 for the α,β and β,γ portions of the ring indicate a small but uniform puckering with respect to the shape of the cyclohexane chair. A Russian publication entitled "Polyhedral Stereoisometry and Pseudorotation in Arsaspirane Systems" has appeared [253].

^{75}As NQR frequencies of twelve cyclic arsenic compounds have been determined and correlated with their structures [254]. The infrared and Raman spectra of 1,3,2-dioxarsenanes have been measured [255]. The frequencies and normal vibrational modes of 2-chloro-1,3,2-dioxarsenane were calculated and compared with those observed for different conformations. The preferred conformation for 1-chloro-1,3,2-dioxarsenane is that of the chair form with the As-Cl bond axial.

Kober [256] has reported on the effect of the gases, *viz*, N_2, H_2, acetylene, isobutane, NH_3, methylamine and ethylamine on the mass spectral fragments formed by chemical ionization of 2-dimethylamino-1,3,2-diox-, -oxathi- and -dithiarsolanes. Ashe, et al., [257] have measured the angular and energy dependence of band intensities in the photoelectron spectrum of arsabenzene. The He(II) photoelectron spectrum of arsabenzene yields additional ionization energies in the region from 17 to 20 eV. The relative intensity changes in the first three bands, compared with their relative intensities in the He(I) spectra, provide support for the previously proposed sequence of states. The results are in excellent agreement with those predicted from theoretical considerations. The He(I) photoelectron spectrum of the heterocyclic system shown below



$Y = N\text{-}CH_3$; $Z = CH_3$; $X = N\text{-}As(CH_3)_2$

has been recorded and interpreted by Kroner et al. [258].

The crystal structures a number of heterocyclic molecules in which arsenic is a heteroatom have been reported. 1,1,3,3,5,5-hexaphenyl-1,3-diphospha-5-

arsatriazine is a planar, six-membered AsNPNPN ring [259]. The structure is disordered and two As-N bond distances of 1.790 Å and an As-C bond distance of 1.91 Å are reported. The 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene molecule is planar, except for the methyl groups [260]. In the 2,6-dimethyl-4,4-diphenyl-1,4-oxarsenonium ion, the arsenic atom is tetrahedral and the mean As-C bond distance is 1.91 Å. The six-membered ring has the chair conformation and the transannular 1,4-As···O distance is 3.10 Å [261].

Using dipole moment measurements, the orientation of phenyl and phenoxyl substituents on the trivalent arsenic atom in 1,3,2-dioxaarsenanes has been investigated [262]. It is concluded from these measurements that the orientation of both groups is axial.

The electrochemical reduction of phenoxarsonium salts in aqueous solution shows that when small alkyl radicals are substituted at arsenic, the reduction involves an irreversible, one-electron step [263]. The reduction of 10-methyl-10-cyclohexylphenoxarsonium iodide occurs in two single electron steps. The reduction occurs with rupture of the arsenic-carbon bond in the side chain and the formation of a tertiary arsine.

XII. Biochemical and Environmental Aspects of Arsenic Compounds

Concern about environmental problems together with a growing interest in the biological role played by trace elements has caused a veritable explosion to take place in the number of publications in this area. The following review is by no means comprehensive and represents a relatively modest fraction of all publications which have appeared.

Reeves [264,265] has reviewed the noncarcinogenic as well as the carcinogenic effects of arsenic (compounds). He points out that As_2O_3 is not a highly toxic compound. Arsenic concentrations reach relatively high levels in shellfish and crustaceans (25-80 ppm). The toxic effects of arsenic poisoning are attributed, at the molecular level, to chemical reactions with sulfhydryl groups on enzymes. Arsenic (compounds not defined) have been shown, experimentally, to display teratogenic effects in animals. Evidence which incriminates arsenic as a carcinogen is based on epidemiologic studies. It has not yet been possible to induce neoplasms experimentally in animals by the use of arsenicals. Pelfrene [266] has also reviewed the subject of arsenic and cancer. He concludes that the question of arsenic carcinogenesis is unsettled. Japanese workers [267] have surveyed the mutation induction capacity of 166 pesticides, including five arsenicals. In their particular bacterial studies their mutagenicities were not detected.

Several arylarsonic acids and their salts have been shown to be phytotoxic [268]. Aryluroniumarylarsonates display high fungicidal activity [269]. Signigicant antifungal and antibacterial activity has been demonstrated for ten ethylarylarsines [270].

Japanese workers have measured the rate of transfer of arsenic (arsenate or arsenite) from the intestine into the circulating blood [271,272]. A strong inhibitory effect on internal absorption was exerted by thiols such as dimercapro thioctic acid, gluthathione and by glucoronolactone.

Arsenic(III) in wine, 4-10 hours after ingestion (in an experiment involving a human subject) causes a five-fold increase in urinary levels of As(III), As(V), methylarsonic acid (MAA) and dimethylarsinic acid (DMAA). The As(III) and As(V) levels decrease and reach normal levels 20 hours after ingestion. However, MAA and DMAA do not reach maximum levels until about 40 hours after ingestion and return to normal levels after about 85 hours. Of the total arsenic ingested, about 50 percent is excreted as DMAA. MAA accounts for 14 percent and As(III) and As(V) about 8 percent, each. The remaining 20 percent is excreted over longer periods of time. This shows that methylation is a primary detoxification mechanism for arsenic in man [273]. Mice exposed to toxic concentrations of arsenic(III) in drinking water excreted 80 percent of it in the form of As(V) after 48 hours. After four days, the proportion of As(V) was more than 95 percent. After eight days, only traces of As(III) were detected [274]. In the Guinea pig, administration of the pharmaceuticals acetarsol, tryparsamide and diphetarsone results mainly in faecal arsenic excretion. On the other hand, in the case of melarsonyl, melarsoprol and arsthinol, the arsenic is eliminated principally by the biliary route [275]. The results of a study very similar to that already described [274] has been published by the same authors [276].

One of the important breakthroughs in arsenic speciation has been the isolation and identification of arsenobetaine from the Australian western rock lobster [277]. Crayfish exposed to waters containing monosodium methylarsonate showed a concentration factor after 56 days of 3.7-3.8 (whole body) greater than that of the environment [278]. Two distinct phases of uptake were noted. An initial phase involves the first 20-30 days and a second uptake phase is involved during the next 30 days.

Parris and Brinckman [279] have measured the rate of oxidation of Me_3As by atmospheric oxygen in methanol and in the gas phase. They conclude that because of its relatively slow rate of oxidation, trimethylarsine can travel considerable distances without undergoing chemical change. This observation has important environmental implications.

Arsenic levels in Indian tobaccos have been found to vary from about 0.4 to 1.0 μg/g [280]. Arsenic contamination was reported in vegetable and soil samples collected in the vicinities of two secondary lead smelters [282]. Unwashed plant foliage was found to possess concentrations about 30 times greater than that of "normal" urban backgrounds. In soil samples collected within 200 meters of the smelters arsenic concentrations were 200 times above "normal." However, samples of edible plants from garden crops grown in home gardens near smelters did not possess abnormal arsenic concentrations. When rice was grown in soil containing 100 ppm of arsenic, a 50 percent decrease in yield was reported [282]. Analysis of soils for arsenic reveals that inorganic arsenic may be found in greater amounts in those portions of the soil that are acid or alkali soluble rather than that which dissolves in distilled water [283]. The distribution of arsenic in wheat following foliar application of sodium methanearsonate has been studied by Domir, et al. [284]. Only 0.2 percent of the leaf application was found in the seeds. Twenty percent was exuded out of the roots into the soil. Over a period of three months, the carbon-arsenic bond remained intact. Benson [285] studied the effect of soil arsenic residues on the growth of apple trees and found that arsenic does retard growth. However, he concluded that it is of minor importance unless the concentrations are very high and that factors other than arsenic are responsible for inhibition of growth.

Sandhu [286] attributed a fish kill to excessive arsenic contents in a reservoir resulting from the use of arsenicals for weed control and cotton defoliation. The bioaccumulation of arsenic by the fish was found to be irreversible. Arsenic residues in animal tissues, vegetation and soils from different locations have been related to those of the surrounding habitat [287]. A report prepared by the Department of the Interior [288] tabulates arsenic concentrations in fish obtained from 100 stations throughout the U.S.

Air samples have been found to contain inorganic arsenic, dimethylarsine and trimethylarsine, but no methylarsine. About 20 percent of the arsenic is converte to the alkylated forms [288].

The bio-transformation of arsenicals is a topic of considerable interest and importance. Phillips and Taylor [289] have isolated 13 strains of *Alcaligenes faecalis* from raw sewage. These organisms are resistant to the toxic effects of arsenite up to 0.01 M and they are able to oxidize arsenite to arsenate. Cox and Alexander [290] have reported that selenite, selenate and tellurate inhibit the conversion of arsenate to trimethylarsine by *Candida humicola*. A meaningful contribution to the function of biological methylating agents in arsenic biotransformations has been made by Cullen, et al. [291]. The microorganisms *Scopulariopsis brevicaulis*, *Candida humicola* and *Gliocladium roseum* when grown aerobically in the presence of L-methionine-methyl-d_3 and arsenic compounds incorporate CD_3 into the evolved methyl arsine(s). This indicates that S-adenosylmethionine or a related sulfonium compound is involved in the biological methylation. The existence of methylated arsenic compounds in western rock lobsters has been clearly demonstrated [292].

Several papers describe the removal of arsenic from its water solutions. A review on the use of activated carbon, ion-exchange and precipitation methods has been prepared by Milovanov [293]. A Russian patent [294] describes a process for the removal of arsenic from water in connection with ore beneficiation. The selective adsorption on silica gel impregnated with ferric hydroxide of arsenite and arsenate has been described [295].

Arsenic does not affect the incidence of white muscle disease in ewes [296].

XIII. Industrial Applications and Miscellaneous

The rate constant for the reaction of $(CH_3)_3As$ with CH_3I in water has been estimated to be $3 \times 10^{-3}\ M^{-1}\ sec^{-1}$ [297]. Crops were grown for three seasons following a single soil-incorporation application of MSMA [$CH_3As(O)(OH)ONa$] [298]. The sensitivity of crops to soil arsenic decreased in the order: snap beans>rice soybeans>potatoes>cotton. The yields of snap beans and rice were proportional to the increase in MSMA application. Soybeans and potato yields were not affected at the lowest concentrations used, 22 and 45 kg/ha, but were reduced at the highest concentration used, 269 kg/ha. Cotton yields were unaffected at all three concentrations. The arsenic contents of the edible portions seldom exceeded twice that of the untreated controls, even at the highest MSMA levels.

Core level binding energies and *LMM* Auger transition energies have been measured for arsenic and a number of its inorganic and organic derivatives [299]. It was concluded that relaxation energy changes derived from binding energy and Auger chemical energy shifts are: independent of coordination number, independent of bond type and are predominantly associated with extra atomic relaxation.

The extraction of Fe(III) from its aqueous solutions by *bis*(n-octyl)arsinic acid in chloroform has been investigated [300]. Arsenic can be separated from copper by extracting it from its aqueous solutions by *tris*(*n*-butyl)phosphate in 2-ethylhexanol [301].

A polymer fiber adsorbent containing arsonic acid groups, ≥ 1 meq/g fiber, and able to adsorb heavy metals, e.g., UO_2^{++}, has been prepared [302]. Arsonium groups have been introduced on a chloromethylated divinylbenzene-styrene copolymer treated with lithium dialkylarsenide followed by quaternization with methyl iodide. The polymer functions as an ion-exchanger [303]. The ion exchanger just described is the subject of a Russian patent [304].

Arsenicals have found a number of catalytic applications. The oxidation of a number of alkenes to the epoxides is catalyzed by $Ph_3As(OH)_2$ [305]. Other arsenic compounds have found use in the conversion of olefins to the epoxides; they are As_2O_3, $As(OEt)_3$, As, As_2O_5, $AsCl_3$, Ph_3As and $PhAsO_3H_2$ [306]. The platinum complex, $[(C_6H_5)_2ClAs]_2PtCl_2$-$SnCl_2$ has been found to catalyze the homogeneous carbonylation of α-olefins to carboxylic acids and esters [307]. The reduction of a nickel salt with Et_3Al in the presence of a ligand such as Bu_3As produces a catalyst for the trimerization of isoprene to $H_2C{=}CMe(CH_2)_3CMe{=}CHCH_2CH_2C({=}CH_2)CH{=}CH_2$ [308]. The catalyst is also the subject of a French patent [309]. The electrochemically initiated polymerization of styrene is most efficiently promoted by the use of arsonium salts as electrolytes [310]. Tetraphenylarsonium salts function as inter-phase transfer catalysts in the preparation of organic isocyanates by the reaction of water-soluble cyanates with organic halides in two phase liquid systems [311]. Organoarsenic compounds of the type R_3M, where R = alkyl, aryl, alkoxy or phenoxy group, function as catalyst stabilizers and eliminate the need for catalyst stabilization during the manufacture of aldehydes by the reaction of olefins with CO and H_2 over rhodium catalysts [312].

A complex which forms between $PdCl_2$ and triarylarsines functions as a catalyst in the preparation of thiol esters by the reaction of alkenes or alkynes with CO and a thiol [313]. Alkoxides of arsenic have been used as coupling agents in the binding of glass fibers to elastomers and thermosetting resins [314]. Compounds of the type R_3AsCuX are able to complex with olefins and have been used to separate complexable ligands from feed streams [315]. Arsonium salts having structures like $Ph_3As^+CH_2CH_2O_2CCl\cdot Cl^-$ can be used to protect NH_2 and OH groups in peptide synthesis [316].

A Russian patent [317] describes the use of the heterocycle, 1-phenyl-2,5-dimethyl-4-arsacyclohexanone methyl iodide as a plant growth regulator. Cotton gloves dipped in a mixture which contains, among other components, 10,10'-oxy*bis*(phenoxarsine) are resistant to bacterial growth [318]. Hydrazono-1,3,2-dithiarsetanes are claimed to possess useful herbicidal, fungicidal, nematocidal and insecticidal properties [319]. Arylarsonium salts such as $[Ph_2(p\text{-}PrC_6H_5)_2As]ClO_4$ are used as antifoggants to suppress fog formation due to impurities, by-products, catalyst residues and the like in the manufacture of silver halide-gelatin emulsions [320].

A Russian patent describes the preparation of bromobiphenylenearsine by heating biphenyl with tribromoarsine in the presence of $AlBr_3$-oleum or $SnCl_4$-oleum catalysts [321]. In the presence of $AlCl_3$ together with $SnCl_4$ and/or oleum, the reaction between $AsCl_3$ and biphenyl yields 9-chlorobiphenylenearsine [322]. The reactions of diphenyl ether with arsenic trioxide between 100-260° in the presence of $AlCl_3$ as a chlorinating agent gives 10-chlorophenoxarsine [323]. Another Soviet patent [324] parallels the one just presented but describes the addition of oleum as another component.

The removal of arsenic from waste waters by electrolytic coagulation is the subject of one publication [325] and a patent issued to the Gulf Research and Development Co. describes the removal of arsenic from gaseous hydrocarbon streams [326]. In the latter case, the arsenic is removed by PbO supported on Al_2O_3. The sorbent contains 20 percent Pb and has a compacted density of 0.084 g/cm^3.

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