ARSENIC

ANNUAL SURVEY COVERING THE YEAR 1972

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1. BOOKS AND REVIEWS

One new book devoted to organoarsenic, -antimony, and -bismuth compounds and several books containing chapters or sections devoted to organoarsenic compounds have appeared in 1972. A supplement to Dub's compilation of organoarsenic, -antimony, and -bismuth compounds has been published [1]. This covers the literature from 1965-1968 and is a non-critical summary of all compounds containing As-C, Sb-C, and Bi-C bonds which have been mentioned in the chemical literature during the time period under consideration.

In a new series of monographs covering inorganic, organic, and physical chemistry and projected to contain thirty-three volumes, Crow and Cullen [2] have written an excellent and up-to-date review of organic compounds of arsenic, antimony, and bismuth. An excellent review article on the use of onium compounds in the synthesis of organometallic (and organometalloid compounds) includes an extensive review of the preparation of organic arsenic compounds [3].

In a short series of monographs dealing with organotin compounds, one chapter is devoted to compounds containing Sn-P, Sn-As, Sn-Sb, and Sn-Bi bonds [4]. The majority of the arsenic compounds also contain As-C bonds. In a review article restricted to organoselenium compounds which contain Se-P, Se-As, and Se-Sb bonds, a number of organoarsenic compounds have been described [5]. King [6] has published a review on ligands containing poly(tertiary phosphines) and poly(tertiary arsines). Most of the pioneer work on these types of compounds has come from King's laboratory. In another review paper on the preparation of organic compounds of metals or metalloids by means of the Grignard reaction, a number of organoarsenic compounds were mentioned [7]. A review article has also appeared dealing with the chemistry, mechanism of therapeutic action, and the preparation of medicinally valuable organoarsenic compounds [8]. In a review paper on radical reactions of the type

$$X^{\bullet} + MR_n \rightarrow XMR_{n-1} + R^{\bullet}$$

(where M is a metal or metalloid, and X is $RO^{\bullet}$, $RS^{\bullet}$, $RSO_2^{\bullet}$, etc.), reactions where M is arsenic have been considered [9].

A review paper on the use of arsenicals in the treatment of *Entamoeba histolytica* has been published [10]. Kaesz and Saillant [11] have reviewed hydride complexes of transition metals. A number of these complexes contain tertiary arsines as ligands.

In a new thirteen volume work entitled *Comprehensive Chemical Kinetics* the kinetics of organoarsenic compounds have been considered. In Vol. 4 [12] the kinetics of pyrolysis of several organic arsenic compounds have been summarized. In Vol. 7 [13] the reactions of several transition metals coordinated to tertiary arsines have been considered.

2. PRIMARY AND SECONDARY ARSINES

The preparation, spectra (IR and NMR), and some reactions (cleavage with HX and alkaline hydrolysis) of a series of new compounds containing As-Si bonds have been the subject of a paper by Anderson and Drake [14]. Some of the reactions employed for preparing these compounds were:

$$n\mathrm{MeAsH_2} + \mathrm{LiAlH_4} \rightarrow \mathrm{LiAl(AsHMe)}_n\mathrm{H}_{4-n} + n\mathrm{H_2}$$

$$n\mathrm{Me_2AsH} + \mathrm{LiAlH_4} \rightarrow \mathrm{LiAl(AsMe_2)}_n\mathrm{H}_{4-n} + n\mathrm{H_2}$$

In the above reactions n is probably 3 as judged by the quantity of H_2 evolve

$$\mathrm{LiAl(AsMe_2)_3H} + 4\mathrm{R_3SiBr} \rightarrow 3\mathrm{R_3SiAsMe_2} + \mathrm{R_3SiH} + \mathrm{LiBr} + \mathrm{AlBr_3}$$

(where R = H or Me)

$$\mathrm{LiAl(AsHMe)_3H} + 4\mathrm{R_3SiBr} \rightarrow 3\mathrm{R_3SiAsHMe} + \mathrm{R_3SiH} + \mathrm{LiBr} + \mathrm{AlBr_3}$$

$$2\mathrm{R_3SiAsHMe} \rightarrow \mathrm{(R_3Si)_2AsMe} + \mathrm{MeAsH_2}$$

$$\mathrm{LiAl[As(SiH_3)_2]}_n\mathrm{H}_{4-n} + 4\mathrm{RX} \rightarrow n\mathrm{(SiH_3)_2AsR} + (4-n)\mathrm{RH} + \mathrm{LiX} + \mathrm{AlX_3}$$

(where R = Me or Me_3Si and X = I or Br)

Other compounds prepared included MeSiAsHPh, $(Me_3Si)_2AsPh$, $(Me_3Si)_2AsMe$, $(Me_3Si)_2As(SiH_3)$, $Me_3SiAsMe_2$ and $Me_3SiAsMe(SiH_3)$.

A preliminary Communication [15] without experimental details described the preparation of compounds of the type $Me_3MAsH(CF_3)$ and $(Me_3M)_2AsCF_3$ (where M is Sn or Ge). The compounds were prepared by the following synthesis:

$$Me_3MP(CF_3)_2 + H_2AsCF_3 \rightarrow Me_3MAsH(CF_3) + HP(CF_3)_2$$

$$Me_3MP(CF_3)_2 + Me_3MAsH(CF_3) \rightarrow (Me_3M)_2AsCF_3 + HP(CF_3)_2$$

The replacement of a $P(CF_3)_2$ by an $As(CF_3)_2$ group was observed by Grobe and Demuth [16]. The reaction involved treating $Hg[P(CF_3)_2]$ with an excess of $HAs(CF_3)_2$:

$$Hg[P(CF_3)_2] + 2HAs(CF_3)_2 \rightarrow Hg[As(CF_3)_2] + 2HP(CF_3)_2$$

A patent covering the preparation of arsinophosphines of the type $R_2P(CH_2)_2AsR'_2$ and $R_2PCH = CHAsR_2$ has been issued [17]. These compounds were obtained by treating unsaturated phosphines of the type $R_2PC \equiv CH$ or $R_2PCH = CH_2$ with a secondary arsine.

The preparation of two new organoarsenicals for use as ligands to various metals has been reported by King and Kapoor [18]. The compounds prepared were $PhP(CH_2CH_2AsPh_2)_2$ and $Ph_2AsCH_2CH_2PPh_2$. Complexes of the first compound with Pd, Pt, Rh, Os, Re, Cr, Mo, Mn, and Fe were reported and a comparison of the arsenical with the corresponding phosphorus compound $PhP(CH_2CH_2PPh_2)_2$ was made.

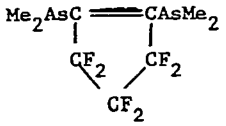
3. TERTIARY ARSINES

A. Preparation

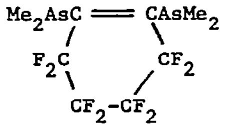
The preparation of trimethylarsine by means of the Grignard reaction has always proved difficult because the arsine is not easily separated from ether. Fournier and Riess [19] have prepared the arsine in the conventional manner and then converted the arsine to the complex $Me_3As \cdot AgNO_3$ by adding aqueous $AgNO_3$ to the ether. After separation of this complex it was converted to the arsine by treatment with thiourea. The authors claimed a 70% yield of the arsine in contrast to a 25% yield by the conventional procedure.

Gol'ding and Sladkov [20] have reported on the reactions of the silver acetylide $PhC \equiv CAg$ with PCl_3, $AsCl_3$, and $SbCl_3$ to give the corresponding ethynylphosphines, -arsines, and -stibines. The yields were 50-70% and the reactions were carried out in benzene-THF in an argon atmosphere.

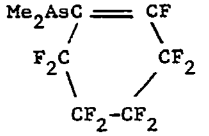
In continuation of previous work on tertiary arsine ligands containing perfluoroalkene groups, Chia and Cullen [21] have reported on the preparation the cyclic compounds I-IV:



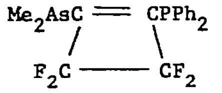
I



II



III



IV

The syntheses involved the reaction between dimethylarsine and a cyclic perfluoroalkene with displacement of HF. Improved syntheses for related compounds which had been described earlier were also given. Both IR and NMR data (^1H and ^{19}F) were given for the new compounds.

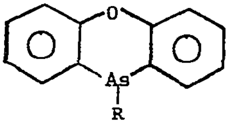
Diphenylmethyl-, diphenylethyl- and diphenylisopropylarsines were prepared by the following reaction [22]:

$$(Ph_2As)_2O+2RMgX \rightarrow Ph_2RAs + MgO + MgX_2$$

The yields by this reaction, however, were small and decreased with increasing size of the alkyl groups. Accordingly, a number of diphenylalkylarsines were prepared from diphenylchloroarsine and the appropriate alkyl Grignard reagent.

The alkyl groups were *n*-C_3H_7, *n*-C_4H_9, *iso*-C_4H_9, *n*-C_5H_{11}, *iso*-C_5H_{11}, C_3H_5, and C_6H_{11}. Some physical constants but no spectral data for the arsines were listed.

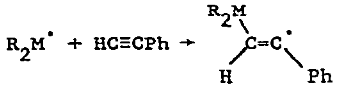
The preparation of the tertiary arsines Et_3As, *n*-Pr_3As, *n*-Bu_3As, Pr_2MeAs, and *n*-Bu_2MeAs by means of the Grignard reaction and their conversion to the corresponding sulfides has been described by Kralichkina, Yambushev, and Gatilov [23]. Gavrilov and coworkers [24] have prepared a series of 10-alkyl-9,10-dihydrophenoxarsines (V) by the reaction of the appropriate Grignard reagent with the 10-chlorophenoxarsine. The 10-phenylethynyl compound, however, was prepared from the 10-chloro compound and the sodium derivative of phenylacetylene.



V

In continuation of earlier work on the reaction of fluoroethylenes with arsenic fluorides, Kopaevich and coworkers [25] have prepared $(C_2F_5)_3As$ by the reaction of $(C_2F_5)_2AsF$ with CF_2=CF_2. Trifluoroethylene and $(C_2F_5)_2AsF$ under pressure and in the presence of SbF_5 gave $(C_2F_5)_2AsCFHCF_3$. The reaction of acetylene with $(C_2F_5)_2AsF$ gave *trans*-$(C_2F_5)_2AsCH$=CHF.

The reaction of diphosphines R_2PPR_2(R= Me, Et, and Ph) and diarsines R_2AsAsR_2 (R= Me and Ph) with phenylacetylene in the presence of UV light or azobis(isobutyronitrile) led to the formation of compounds of the type $R_2MC(Ph)$=$CHMR_2$ (M=P or As) [26]. In the case of $Me_2AsC(Ph)$=$CHAsMe_2$ the ^1H NMR spectra indicated that the compound contained about 10% of the *cis*-isomer and 90% of the *trans*-isomer. A mechanism for the reaction was suggested which involved formation of R_2P or R_2As radicals which reacted with phenylacetylene with the formation of the *trans*-vinyl radicals VI predominating.



$$R_2M^{\bullet} + HC\equiv CPh \rightarrow (R_2M)(H)C=C^{\bullet}(Ph)$$

VI

The *cis*- and *trans*- mixture of $Me_2AsC(Ph)=CHAsMe_2$ reacted with methyl iodide to form a dimethiodide.

The reaction of Mannich bases of the type $p\text{-}XC_6H_4COCHR'CHR''NR_2$ (where NR_2 was piperidine) with secondary phosphines and arsines has been described by Tzschach and Kellner [27]. Thus diphenylarsine and dicyclohexylarsine reacted with $C_6H_5COCH_2CH_2NC_5H_{10}$ to give $C_6H_5COCH_2CH_2AsR_2$ (R= Ph or cyclohexyl). Dicyclohexylarsine reacted in a similar manner with the Mannich base substituted with a p-Br or p-CH_3 on the phenyl ring. However, diphenylarsine reacted with p-substituted Mannich bases in a different manner:

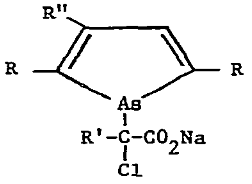
$$p\text{-}XC_6H_4COCH_2CH_2NC_5H_{10} + 2Ph_2AsH \rightarrow p\text{-}XC_6H_4COCH_2CH_3 + (Ph_2As)_2 + HNC_5H_{10}$$

(where X = CH_3, Br, or OCH_3).

A number of reactions of the arsenic- and phosphorus-substituted propiophenones with such reagents as H_2O_2, S, hydroxylamine, and 2,4-dinitrophenylhydrazine were described and the resulting compounds characterized by elemental analysis.

Mannich bases with phenyl substituents in the α-position to the carbonyl group did not react with Ph_2PH or Ph_2AsH, but the corresponding sodium compounds Ph_2PNa and Ph_2AsNa did react to give compounds of the type $PhCOCH(Ph)CHR'PPh_2$ and $PhCOCH(Ph)CHR'AsPh_2$ (where R' = H or Ph).

Märkl and coworkers [28] have suggested a general method for the preparation of aryl-substituted arsenins which involves an intramolecular carbene insertion. Thus arsoles of the type VII were prepared by the reaction of sodium trichloroacetate or sodium phenyldichloroacetate with the appropriately substituted 1-lithioarsole.



VII (a-d)

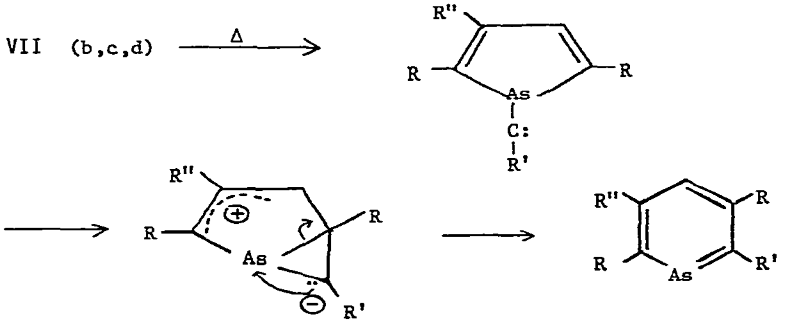
a R = Ph, R' = Cl, R'' = H

b R = naphthyl, R' = Ph, R'' = H

c R = Ph, R' = Ph, R'' = Ph

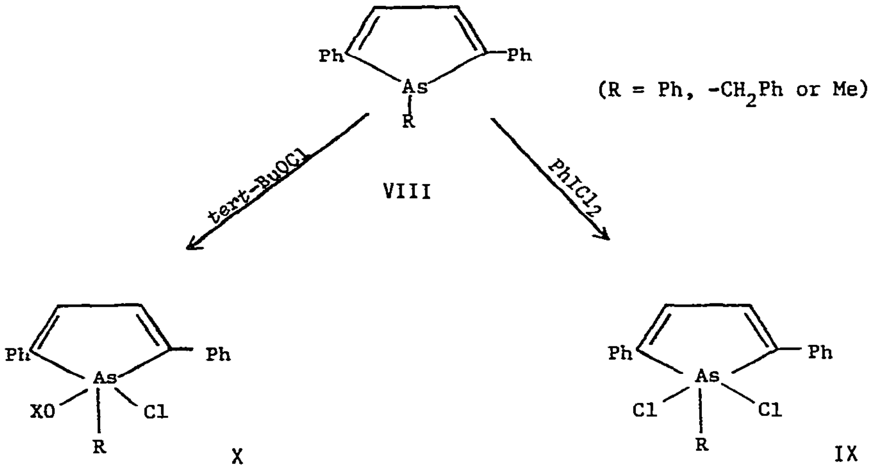
d R = Ph, R' = Ph, R'' = H

The compound VIIa degraded in an undefined manner at 170°, whereas the remaining three compounds gave phenyl-substituted arsenins via loss of NaCl and CO$_2$ and insertion of the resulting carbene into the arsole ring system.



In the case of the unsymmetrical arsole VII c, two isomeric arsenins are predicted but only one compound has been isolated in a pure state. The ^{1}H NMR and UV spectra of the arsenins were listed and discussed.

In an interesting paper devoted to reactions of 1-substituted 2,5-diphenyl arsoles, Märkl and Hauptmann [29] state that the less pronounced nucleophilic character of tertiary arsines compared with phosphines is further reduced in the aromatic arsole system. Thus 1,2,5-triphenyl- and 1-phenyl-2,5-dimethyl arsoles do not form quaternary salts or sulfides, and oxidation with H_2O_2 yields oxides in only moderate (but unstated) yields. However, the reaction of arsoles of the type VIII with $PhICl_2$ gave the dichlorides IX, and *tert*-butyl hypochlorite gave X.



(R = Ph, $-CH_2Ph$ or Me)

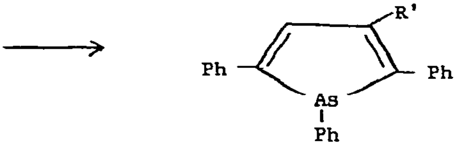
VIII

X

IX

Further reactions of IX and X were also described. One interesting reaction of X involved the formation of 3-substituted arsoles by the reaction of X with organolithium reagents:

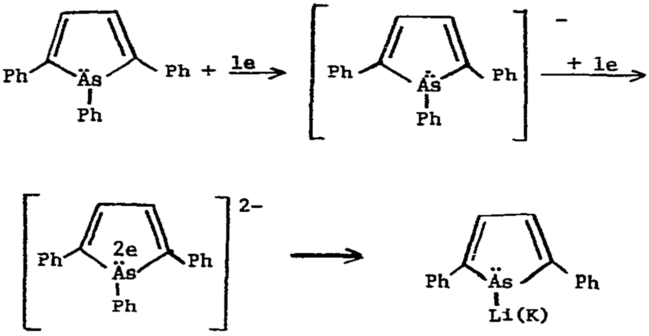
X (R = Ph) + R'Li



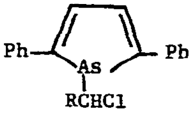
(R' = Me, Ph, $C_6H_4NMe_2$)

The authors suggest that the bulky *tert*-butyl group blocks a nucleophilic attack on the As atom and thus induces an S_n2' substitution and subsequent rearomatization by elimination of *tert*-butyl alcohol.

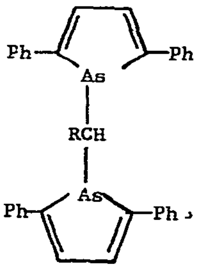
Märkl and Hauptmann [30] have reported on the cleavage of As-substituted 2,5-diphenylarsoles by alkali metals. Thus 1,2,5-triphenylarsole reacts with Li or K in dimethoxyethane in a stepwise manner to give first a radical anion and then an alkali arsenide:



The ESR spectrum of the radical anion was given. The dianion could not be detected. Reaction of the radical anion or the Li or K arsenides with alkyl halides gave 1-alkyl-2,5-diphenylarsoles. In the case of 1-(*p*-dimethylaminophenyl)-2,5-diphenylarsole, an attempt to detect the dianion by treatment of the arsole with two equivalents of alkali metal followed by deuterolysis gave dimethylaniline which contained no deuterium. Reactions of the radical anion from 1,2,5-triphenylarsole with CH_2Cl_2 or $C_6H_5CHCl_2$ gave both the monochloroalkylarsoles (XI) and also the coupled products (XII).



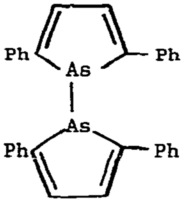
XI



XII

(R = H or Ph)

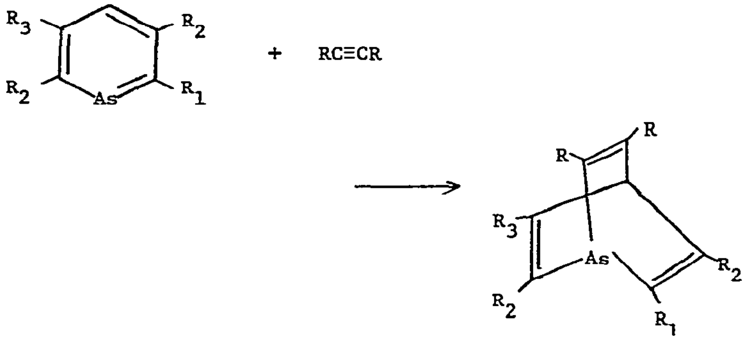
The reaction of the radical anion from 1,2,5-triphenylarsole or of 1-lithio- or 1-potassio-2,5-diphenylarsole with trityl perchlorate led to the formation of XIII.



XIII

In contrast to the triphenyl compound, 1-methyl-2,5-diphenylarsole reacted with two equivalents of alkali metal to form a stable dianion.

Triphenyl- and tetraphenyl-substituted arsenins were found to react with substituted acetylenes to give bicyclic compounds of the type XIV [31]. A similar type of Diels-Alder reaction has been observed by Ashe and Gordon [31a] and is discussed under Bismuth.



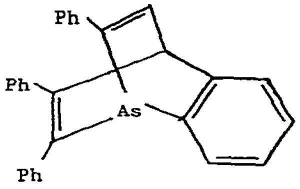
XIV

where $R_1 = R_2 = R_3 = Ph$, $R = CF_3$

$R_1 = R_2 = Ph$, $R_3 = H$, $R = CN$

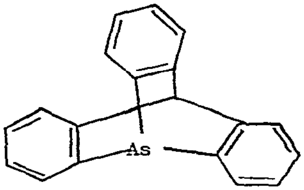
$R_1 = R_2 = Ph$, $R_3 = H$, $R = CO_2Et$

The triphenyl arsenin was also found to react with benzyne (generated from diazotized anthranilic acid) to give XV.

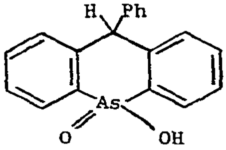


XV

The preparation of the interesting heterocycle arsatriptycene (XVI) has been described by Vermeer and coworkers [32]. The compound was obtained as the oxide by heating *o*-$Ph_2CHC_6H_4AsO_3H_2$ with polyphosphoric acid. It was also possible to isolate 5-hydroxy-10-phenyl-5,10-dihydrodibenz[b,e]arsenin 5-oxide (XVII) from the reaction mixture in 18.9% yield when the reaction was run for only 80 min. The arsatriptycene oxide was readily reduced to XVI by sulfur dioxide. It gave a series of arsonium salts when treated with MeX(X= I, Cl, FSO_3, and *p*-$CH_3C_6H_4SO_3$). The UV spectrum of arsatriptycene was reported and considered in some detail.



XVI



XVII

An East German patent covers the preparation of benzoylalkylarsines of the type $R_2AsCH_2CH_2COR'$, $R_2AsCH_2CHPhCOPH$, and similar types of compounds [33] In these compounds R = Ph or cyclohexyl and R' = phenyl or a substituted phenyl.

B. Spectra

Preer, Tsay and Gray [34] have reported on the UV spectrum of *o*-phenylenebis(dimethylarsine), the UV spectra of several arsine charge-transfer complexes with tetracyanoethylene as well as charge-transfer complexes of Ph_3N and Ph_3P with this same acceptor and the ESR spectra of several arsines after UV photolysis. The electronic spectrum of *o*-phenylenebis(dimethylarsine) was run at 77°K and 300°K and assignments of the absorption bands were made. Tetracyanoethylene formed simple 1:1 charge-transfer complexes with several arsines; stability of the complexes was solvent dependent. UV photolysis of various arsines at 96°K yielded thermally labile, paramagnetic products.

Brill and Long [35] have compared the NQR spectra of a series of *o*-, *m*- and *p*-substituted triarylarsines and triarylstibines. There is a linear correlation between the ^{75}As NQR frequencies and the Taft σ_R° resonance parameters for the *p*-substituted (but not the *m*-substituted) compounds. These results suggest that the most efficient means of transmission of the substituent electronic effects is through the π-system. The NQR data suggested that the mechanism of this transmission is $\pi(p\text{-}p)$ rather than π $(p\text{-}d)$. Quite different results were obtained with *p*-substituted triarylstibines. Here there is a linear correlation between the $^{121,123}Sb$ NQR frequencies and Hammett substituent constants, but not σ_R° or σ_I parameters. The authors suggest that because of the larger size of the antimony atom compared with the arsenic atom, there is more of a mismatch between *p* and/or *d* orbitals used in π interaction and the antimony atom may therefore not feel the π-system effects as well, and changes in the σ and π network could become more competitive.

In a paper devoted to the vibrational spectra of compounds of the type $M(C{\equiv}CMe)_4$ (M=Si, Ge, or Pb) and $M(C{\equiv}CMe)_3$, (M=P, As, or Sb), the Raman spectrum of $As(C{\equiv}CMe)_3$ in the solid state and the IR spectra of this same compound in solution (CCl_4 and CS_2) and in the gaseous state were determined [36]. It was assumed that the compound possessed C_{3V} symmetry and assignments for all of the observed frequencies were made.

The IR and Raman spectra of the three compounds $(CF_3)_3P$, $(CF_3)_3As$, and $(CF_3)_3Sb$ have been reported [37], and a normal coordinate analysis was performed. It was found that the stretching force constants for the compounds were somewhat smaller than those of the corresponding methyl compounds.

Shagidullin and coworkers [38] have reported on the IR spectra of a large series of arsenic-containing alkynes of the type $R_2AsC{\equiv}CH$, $R_2AsC{\equiv}CR'$, and $R_2AsC{\equiv}CAsR_2$. Introduction of an arsenic group in the α-position to the $-C{\equiv}C$ grouping substantially lowers the frequency of vibration of the $C{\equiv}C$ group which the authors suggest may be due to interaction of the π-electron system of the acetylenic linkage with *d*-orbitals of the arsenic atom. The fact that $\nu_{C{\equiv}C}$ comes at much lower frequencies for arsenic than for the corresponding phosphorus compounds was explained by the increased mass of the arsenic atom.

Laskorin and Yakshin [39] have prepared a series of acyl derivatives of P, As, and Sb of the type of $MeC(O)XR_2$, where X is P, As or Sb for comparison of their properties with those of the corresponding amides, $MeC(O)NR_2$. The compounds were obtained by reaction of ketene with the necessary hydrides of P, As or Sb. The P, As, and Sb acyl derivatives differed considerably from amides in that they reacted vigorously with atmospheric oxygen to yield oxides. They also reacted with alkyl halides to form onium compounds, with metal salts to form complexes and with sulfur and bromine to form sulfides and bromides. The UV and PMR spectra, and the IR frequencies of the carbonyl groups are given.

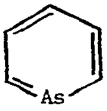
The δ values of the PMR spectra did not serve as a quantitative measure of the influence of the carbonyl group on the electron density distribution in the acyl P, As, and Sb compounds. Qualitative differences between amides and these aryl compounds were more manifest in the excited state as shown by their UV spectra.

The authors conclude that both spectral and chemical properties of the P, As and Sb compounds differed from the amides as a result of hindrance of p_π-p_π-conjugations with the former compounds. The spectral properties of the carbonyl groups in the P, As, and Sb compounds differ from the C=O grouping in aldehydes and ketones both in the ground and excited state which the authors suggest may be due to conjugation of the carbonyl group with higher vacant orbitals of the hetero atoms.

In the first paper of a series to be devoted to the mass spectrometry of organic compounds of Group V elements, Kostyanovsky and Plekhanov [40] compare the mass spectra of a number of straight chain aliphatic derivatives of the Group V elements. The mass spectra of the arsenicals Me_3As, Et_3As, Bu_3As, $(n\text{-}C_5H_{11})_3As$ and $(n\text{-}C_6H_{13})_3As$ are given. In addition the mass spectrum of Et_2AsBr was determined. The principal conclusion of the paper was that α-cleavage, the main cleavage path of amines, was not typical for P, As, Sb, and Bi derivatives. A similar paper by Kostyanovskii and coworkers [41] giving essentially the same experimental work has appeared in the Russian literature.

In a paper by Lyons and Symons [42] the ESR spectrum of γ-irradiated triethylarsine was shown to contain seven hyperfine components separated by about 450 G. The results were indicative of two equivalent interacting arsenic atoms, and an analysis of the hyperfine tensor components suggests that the species is the dimer cation $(Et_3AsAsEt_3)^+$.

In a paper devoted to the photoelectron spectra of phosphorin and arsenin (XVIII), Schäfer and coworkers [43] demonstrated that in these two systems the π-MO with the non-zero coefficient on the heteroatom was higher in energy than the π-MO with its node on the hetero atom. These results are in contrast to those obtained with pyridine.



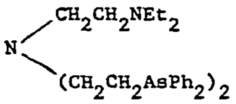
XVIII

In a paper devoted to the ^{57}Fe and ^{121}Sb Mössbauer spectra of compounds of the type $Ph_3MFe(CO)_4$ and $(Ph_3M)_2Fe(CO)_3$ (where M= P, As, and Sb), Bowen and coworkers [43a] have compared the Mössbauer parameters of these compounds at 80 and 295°K based on the ^{57}Fe results. Based on the assumption from the ^{121}Sb Mössbauer results that the M-Fe bond is primarily a σ-bond, they conclude that Ph_3Sb is the weakest σ donor, and Ph_3P is the strongest. This paper is discussed in greater detail under Antimony.

Borisova and Petrov [44] have contributed a quantum-mechanical paper on the electronic structure of the triphenyl derivatives of the Group VA elements. Using both the simple Hückel MO method and the Pople-Sentry method, and by a method considering *d*-orbitals of the central atom, they have calculated spectral characteristics of the compounds. They concluded that both chemical and optical properties of the compounds have to be interpreted by two electronic effects acting in opposite directions, namely the donating effects of the lone pair on the central atom and the negative inductive σ-effect which is determined by the electron accepting properties of the empty d-orbitals.

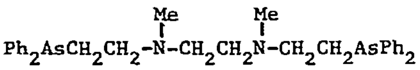
C. Use as Ligands

The preparation of three new tertiary arsines for use as ligands in coordination chemistry was the subject of a paper by Sacconi and Gatteschi [45]. The new ligands were XIX, XX and XXI.



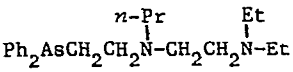
$N(CH_2CH_2NEt_2)(CH_2CH_2AsPh_2)_2$

XIX



$$Ph_2AsCH_2CH_2\text{-}\overset{\overset{Me}{|}}{N}\text{-}CH_2CH_2\overset{\overset{Me}{|}}{N}\text{-}CH_2CH_2AsPh_2$$

XX



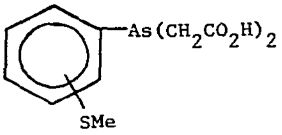
$$Ph_2AsCH_2CH_2\overset{\overset{n\text{-}Pr}{|}}{N}\text{-}CH_2CH_2\overset{\overset{Et}{|}}{N}\text{-}Et$$

XXI

The ligands were prepared from $Ph_2AsK\cdot 2dioxane$ and the appropriate chlorides. A number of complexes of these ligands with various nickel compounds were described, and their IR spectra were given.

In a paper by Bennett, Bruce, and Stone [46], the preparation of benzyldimethylarsine from dimethyliodoarsine and benzylmagnesium chloride was described. The arsine reacted with a stream of air to form dimethylarsinic acid. The NMR spectra of the compounds formed from the arsine and various compounds of Mn, Fe, Ru, Rh, Pt, and Pd were described.

A number of new ligands have been prepared by Ford and coworkers [47]. These ligands contained sulfur or arsenic atoms or both as the donor atoms of the molecules. The three isomeric bis(carboxymethyl)(methylthiophenyl)-arsines (XXII) were prepared by conventional syntheses.



XXII

o-Phenylenebis[di(2-carboxyethyl)arsine] was obtained by the following synthesis:

$$o\text{-}H_2O_3AsC_6H_4NH_2 \xrightarrow[2.\ As_2O_3/KOH]{1.\ NaNO_2}$$

$$(o\text{-}H_2O_3As)_2C_6H_4 \xrightarrow[Hg]{Zn/HCl}$$

$$(o\text{-}H_2As)_2C_6H_4 \xrightarrow{CH_2{=}CHCN} o\text{-}C_6H_4[As(CH_2CH_2CN)_2]_2 \xrightarrow[2.\ HCl]{1.\ KOH} o\text{-}C_6H_4[As(CH_2CH_2CO_2H)_2]_2$$

By a somewhat similar synthesis 1,2-bis[phenyl(2-carboxyethyl)arsino] ethane

$$HO_2CCH_2CH_2As(Ph)CH_2CH_2As(Ph)CH_2CH_2CO_2H$$

was obtained. All of these ligands were complexed with Ag, Cu(II), Ni, Zn, and Cd and the complex formation constants were determined.

The reaction of the two acetylenes $Ph_2PC{\equiv}CCF_3$ and $Ph_2AsC{\equiv}CCF_3$ with $Fe_3(CO)_{12}$ in benzene led to the formation of the compounds $(C_{15}H_{10}PF_3)_2$-$Fe_3(CO)_8 0.5C_6H_6$ and $(C_{15}H_{10}AsF_3)_2Fe_3(CO)_8 0.5C_6H_6$ [48]. The structure of the phosphorus compound was determined by X-ray data, and the arsenic anolog is believed to have a similar structure, but unlike the phosphorus compound there was no evidence for bridging Ph_2As groups in the mass spectral data.

Cullen and coworkers [49] have prepared the following ditertiary arsines: $Me_2AsCH_2CH(SiMe_3)AsMe_2$, $Me_2AsCH_2CH(SiCl_3)AsMe_2$, $Me_2AsCH_2CHFAsMe_2$, Me_2AsCF_2-$CHFAsMe_2$, $Me_2AsCH_2CHClAsMe_2$ and $Me_2AsCH_2CH(CN)AsMe_2$. The coordination compounds of these arsines with chromium carbonyl were then prepared, and the geometry of these complexes was elucidated by means of ^1H NMR spectra.

Mann and coworkers [50] have reported on the use of ^{13}C NMR for determining the stereochemistry of tertiary phosphine and arsine complexes of transition metals. Thus the complexes $IrCl_2(CO_2Me)(CO)(AsMe_2Ph)_2$ and $IrCl_2(CH_2C(Me){=}CH_2)(CO)(AsMe_2Ph)_2$ were both assigned the structure with the two arsenic ligands trans on the basis of two different arsenic methyl signals since there was no plane of symmetry along the As-Ir bond in the octahedral complex.

In an interesting paper, Rowe, McCaffery, and coworkers [51] have compared the absorption spectra and the MCD of a series of iridium complexes of the type $IrCl_4L_2$, where L = PR_3, $AsPr_3$, Et_2S and pyridine. They found that the energy of the L-Ir charge transfer transition occurs at 9010cm^{-1}

for L=$AsPr_3$ 9400cm^{-1} for L-PR_3, 15,100cm^{-1} for L=Et_2S, and 22,000-25,000cm^{-1} for L=pyridine. They conclude that the L→M transition parallels the reducing power of the ligand and may reflect the energy of the L σ-bond orbitals relative to the metal. The formation of high-energy low-lying excited states for phosphines and arsines may be responsible for the "softness" of these ligands.

Compounds with gallium-arsenic bonds, *viz.* $Me_3GaAsEt_3$, $Et_3GaAsEt_3$ and $Et_2GaClAsEt_3$, were prepared by mixing the components at room temperature. The products were purified by distillation *in vacuo* or by recrystallization [52].

A U. S. patent described the use of tertiary phosphines or arsines ($R^1R^2R^3As$) coordinated to metals to form complexes which produce luminescence when photoexcited with 3000-4000 A light [53]. The metals used were Ni^o, Pd^o, Pt^o, Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Th^{3+}, or In^{3+}.

A large number of papers describing the use of tertiary arsines as ligands have been published. The metals coordinated to the arsenic in the complexes include chromium [54-59], cobalt [60-70], copper [62, 71-73], gold [74,75], iridium [76-85], iron [46,48,70,86-94], manganese [46,95-99], mercury [100-102], molybdenum [54,55,57-59,103-108], nickel [60,64,66,67, 109-119], osmium [120-122], palladium [46,112,113,123-131], platinum [46, 90,112,113,123,126,132-141], rhenium [95,142], rhodium [46,143-147], ruthenium [46,121,148-156], silver [157,158], tin [159,160], and tungsten [54,57-59,103,105,106,161-163].

D. Other Chemical and Physical Properties

In an earlier paper from Mislow's laboratory it had been reported that the barrier to pyramidal inversion at phosphorus is markedly lowered when a silyl group is substituted on the phosphorus atom. This observation has now been extended to arsenic compounds with similar results [164]. Thus the inversion barrier is lowered by 18 kcal. in isopropylphenyltrimethylsilylarsine as compared with ethylmethylphenylarsine. The authors then compare the barrier to inversion of such compounds as $Ph(CHMe_2)MYMe_3$, where M is P or As and Y is Si, Sn or Ge. They found a linear correlation between the electronegativity of the element Y and the inversion barrier. On the basis of these results the authors suggest that there is no need to invoke (p-d)π conjugation as a source of the observed barrier lowering. It should be noted, however, that Allred electronegativities were used (Si = 1.90, Ge = 2.01 and Sn = 1.96) and it is doubtful if their conclusions are justified from such small and questionable differences in electronegativities.

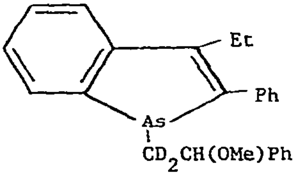
When two silicon atoms are substituted on P or As, $PhP(SiHMe_2)_2$ and $PhAs(SiHMe_2)_2$, the barrier to inversion is again markedly lowered as compared with substitution by only one silicon.

In a paper dealing with the barrier to inversion of a number of pyramidal compounds or ions such as phosphines, amines, carbanions, oxonium ions, etc., tertiary arsines are among the compounds considered [165]. From the plot of the inversion barriers of phosphines against the inversion barrier of identically substituted arsines it was concluded that arsines were less sensitive to a given structural change than phosphines. The original paper should be consulted for the conclusions of the authors on the various free energy correlations with barriers to pyramidal inversion.

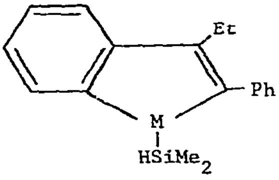
In 1954 Weston [166], on the basis of force-field calculations, predicted the barrier heights to inversion of Me_3P, Me_3As, and Me_3Sb as 22.0, 29.2 and 26.7 kcal/mol, respectively. It was later shown that the barrier to inversion of methyl-*n*-propylphenylphosphine was 28-30 kcal/mol. Senkler and Mislow [167] have now reported that the barrier to inversion of ethylmethylphenylarsine was 42.4 ± 0.5 kcal/mol at 217.6°.

In a preliminary communication, the synthesis of the arsindole XXIII has been reported by Bowman and Mislow [168]. The compound was oxidized to its oxide with H_2O_2 and the mixture of diastereomers enriched in one diastereomer by column chromatography. The enriched mixture was then reduced stereospecifically with phenylsilane to give a 72:28 diastereomeric mixture of the arsindole. Equilibration of this mixture at 151.1° in 20 vol% toluene-d_8 gave a first order rate constant from which a $\Delta G^{\ddagger}$ for pyramidal inversion was calculated as 35.2 kcal/mol. This value was considerably lower than that for the acyclic arsine MeEtPhAs, for which a $\Delta G^{\ddagger}$ value of 43.1 kcal/mole had previously been found. From this result the authors concluded that the lone pair on arsenic was involved in cyclic (4*p*-2*p*)π delocalization and that the planar arsole ring could be regarded as aromatic. A similar effect had previously been found for the corresponding phosphorus compound.

The authors [168] also prepared the two silyl compounds XXIV and found a marked decrease in the barrier to pyramidal inversion.



XXIII



XXIV

(M = P or As)

Gatilov and coworkers [169] have resolved *n*-butylethyl-*p*-carboxyphenylarsine by means of its morphine salt. The following tertiary arsines were resolved by means of their quinine salts: methyl-*p*-bromophenyl-*p*-carboxyphenyl, ethyl-*p*-bromophenyl-*p*-carboxyphenyl, and ethylphenyl-*m*-carboxyphenyl. Both enantiomers of all of these arsines were then oxidized with dinitrogen tetroxide to give the optically active arsine oxides. These compounds were optically unstable and rapidly racemized in the presence of traces of moisture. It was found [170] that when (*m*- or *p*-BrC_6H_4)(p-MeC_6H_4)EtAs was oxidized by $KMnO_4$ the optical activity of the resulting (p-BrC_6H_4)(p-HO_2C-C_6H_4)EtAs (after resolution via its quinine salt) was lower than that of (m-BrC_6H_4)(p-$HO_2CC_6H_4$)EtAs.

Yambushev and Gatilov [171] have also reported that there is a decrease in optical activity in going from o- to p-isomers when tertiary arsines of the type (o-, m- or p-$HO_2CC_6H_4$)EtPhAs are treated with sulfur to give the tertiary arsine sulfides. In all cases, however, the relative configuration and sign of rotation was retained. The $[\alpha]_D^{20}$ values for (o- and m-$HO_2CC_6H_4$)-EtPhAsS, and (m- and p-BrC_6H_4)(p-$HO_2CC_6H_4$)EtAsS were given.

By the use of differential thermal analysis Gatilov [172] has studied the oxidation of the enantiomers of p-carboxyphenylethylphenylarsine by either hydrogen peroxide or by air to give p-$HO_2CC_6H_4$EtPhAsO. Gatilov [173] has also reported on the configuration of tertiary arsine enantiomers during a series of chemical conversions. Thus (+)-EtPhAs$C_6H_4CO_2H$-p, when heated with sulfur in C_6H_6, gave (+)-EtPhAs(S)$C_6H_4CO_2H$-p with retention of configuration. When this sulfide was heated with PhCOEt in C_6H_6, (-)-Ph-(EtS)As$C_6H_4CO_2H$-p was obtained. This sulfide, when heated with EtBr gave (+)-BrPhAs$C_6H_4CO_2H$-p, which with EtMgBr gave the orginal (+)-EtPhAs$C_6H_4CO_2H$-p.

The electrochemical reduction of the m- and p-nitrosubstituted organoarsenicals $Et_2AsC_6H_4NO_2$, $Et_2As(O)C_6H_4NO_2$ and $Et_2As(S)C_6H_4NO_2$ was reported by Vafina and Mil'nikov [174]. The reaction proceeded by a 1-election reduction followed by a 3-electron reduction and only the reduction of the nitro group was effected. In EPR studies it was shown that the hyperfine-splitting constants in As(V) radical ions exceeded those in arsine radical ions.

In a paper devoted to the electron donor capacity of such elements as O, S, Se, Te, N, and As and of π-electron systems (all in their capacity to form intermolecular hydrogen bonds with various acceptor molecules), compounds of the type $R_1R_2R_3As$ are included [175].

In a paper devoted to the solution chemistry of fluorosulfonic acid Paul and coworkers [176] included triphenylarsine among the several compounds studied in this solvent. In contrast to $AsCl_3$, which is a non-electrolyte in fluorosulfonic acid, Ph_3As forms a conducting solution in this solvent. Triphenylarsine is oxidized in HSO_3F by Cl_2, Br_2 and ICl. Curves of the plot of conductivity vs molar ratio of oxidant/reductant are given for all three oxidizing agents. The oxidation with ICl is believed to occur as follows:

$$Ph_3As + 2ICl + HSO_3F \rightarrow Ph_3\overset{+}{As}Cl + I_2 + HCl + SO_3F^-$$

Kustan, Smith and coworkers [177], in study of the reactions of thionyl chloride and sulfur dichloride with triphenylphosphine, -arsine, and -stibine, have reported that triphenylarsine reacts with thionyl chloride with transfer of chlorine to arsenic and the formation of S and SO_2:

$$Ph_3As + SOCl_2 \rightarrow Ph_3AsCl_2 + 1/2S + 1/2SO_2$$

The sulfur then reacts with Ph_3As to give Ph_3AsS. Triphenylarsine reacts with sulfur dichloride to give Ph_3AsCl_2 and either Ph_3AsS or sulfur.

In an article on hydrogen-bonded complexes of phenols with alkylated compounds of a number of elements, alkylarsines are among the compounds studied [178].

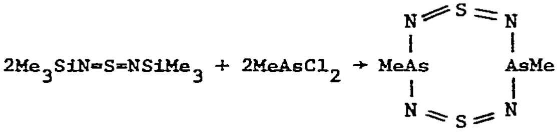
It has been found that tri-*o*-anisylarsine is quaternized by benzyl bromide nearly 100 times faster than triphenylarsine and more than 10 times faster than tri-*p*-anisylarsine [179]. The explanation offered for this fact is that there is $(p\text{-}d)\pi$ overlap between the 2p electrons of the *o*-anisyl oxygen and an empty *4d* orbital of arsenic in the transition state of the S_n2 reaction, thus increasing electron density on the arsenic atom. The authors of this article then argue that such an effect may also occur in the ground state of the arsonium bromide. In accordance with this suggestion they find that the ^1H NMR of the benzyl protons in benzyltri-*o*-anisylarsonium bromide occurs at a much lower δ value than several closely related benzyltriarylarsonium bromides. This deshielding of the benzyl protons, they suggest, is a result of (*p*-*d*)π overlap.

The dipole moments of a number of charge transfer complexes formed between iodine and various donor molecules were determined by Dwivedi [180]. Triphenylarsine was one of the compounds investigated. By means of spectroscopic and thermodynamic data, charge transfer parameters were calculated and it was concluded that triphenylarsine is a powerful donor with 40% charge transfer to iodine in the ground state (compared with 15% for Ph_3N, a weak donor).

The use of di-tertiary phosphines or arsines as well as palladium salts for the preparation of alkenylamines by the reaction of primary or secondary amines with conjugated dienes has been described in a Japanese patent [181]. Thus aniline, 1,3-butadiene palladium acetate and ethylenebis(diphenylphosphine) gave N-(1-methyl-2-propenyl)aniline and N-2-butenylaniline. The arsenical mentioned as a successful catalyst was $Me_2As(CH_2)_2$-$AsPh_2$.

4. AMINOARSINES

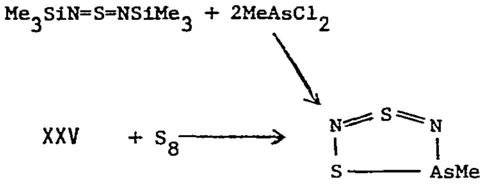
The reaction of methyldichloroarsine with N,N'-bis(trimethylsilyl)-sulfur diimide yielded the interesting heterocycle XXV [182]:



XXV

The compound was characterized by elemental analysis, molecular weight determinations as well as by ^1H NMR, IR, UV, and mass spectrometry.

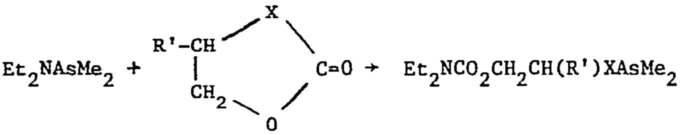
The heterocyclic compound XXVI has also been obtained in poor yield by the reaction of N,N'-bis(trimethylsilyl)sulfur diimide with dichloromethyl arsine in a ratio of 1:2, or by treating XXV with S_8 [183]:



XXVI

The spectra (UV, IR, mass and ^1H NMR) of compound XXVI were given.

It has been shown by Koketsu and coworkers [184] that both cyclic carbonates and thiolocarbonates undergo insertion reactions with diethylaminodimethylarsine:



(where X = O or S)

The structure of the products was determined by spectroscopy, by elementary analysis, and by a study of the degredation products.

In a paper devoted to the reactions of bis(4-lithiophenyl)methylamine the new compound $(p\text{-}Ph_2AsC_6H_4)_2NMe$ was prepared [185]. The starting material was obtained from bis(4-bromophenyl)methylamine and *n*-Buli, and the arsenic compound was obtained in 35% yield from the lithium compound and diphenylchloroarsine.

5. HALOARSINES

The structure of 10-chloro-5,10-dihydrophenoxarsine has been determined by means of a single crystal X-ray diffraction study [186]. Each benzene ring and the two atoms bonded to it are coplanar within 0.04A, and the angle of fold at the As-O line is 156.3°. A comparison of this compound with the corresponding phenarsazine compounds suggests that the phenoxarsine has less aromatic character.

Both the IR and Raman spectra of liquid Me_2AsI have been recorded and assignments of the various bonds have been made [187]. Since the 24 normal modes were not all observed, a normal coordinate analysis was carried out in order to predict the frequencies of the fundamental modes of vibration.

Saraswathi and Soundararajan [188] have calculated the charge distributions and the dipole moments of a number of organophosphorus and organoarsenic compounds. Differences in observed and calculated dipole moments in alkylhaloarsines have been explained in terms of d_π-p_π back-bonding and hyperconjugative effects. The difference between experimentally determined and calculated moments was found to increase in the order bromo-< chloro-< fluoroarsines which was in accord with the strength of the d_π-p_π back-bond in these compounds. In both Me_2AsI and $MeAsI_2$ the calculated moments were less than observed moments which the authors suggest is due to the fact that the mesomeric or hyperconjugative effect of the methyl group outweighs any d_π-p_π back-bonding.

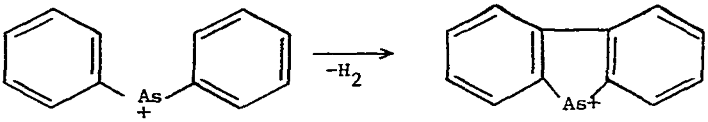
A Japanese patent [189] covers the preparation of alkyl tin halides in which various organic arsenicals such as triphenylarsine, or alkyl-, or aryldihaloarsines acted as catalysts for the reaction.

A patent covering the preparation of 10-chlorophenoxarsine from diphenyl ether, arsenic(III) oxide, and aluminum chloride has been issued [190].

6. OTHER TRIVALENT ARSENIC COMPOUNDS

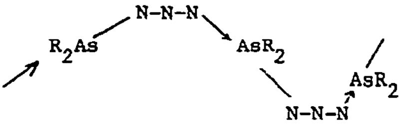
The mass spectra of several trivalent organoarsenic compounds of the type Ph_2AsX, where X = SCOPh, $SCOC_6H_4OMe$-*o*, $SCSNEt_2$ and $OAsPh_2$, as well as the mass spectrum of the pentavalent arsenic compound Ph_2AsO_2H have been reported by Tou and Wang [191]. Because of the similaries between pyrolytic reactions and electron impact induced ion fragmentations, pyrolysis studies were also carried out on these compounds.

The trivalent compounds all gave molecular ions and common fragments at m/e 229, 227, 154, 153, 152, 151, 77, and 51. It is believed that the ion m/e 229 undergoes an *ortho* coupling to give the ion at m/e 227:



It was suggested that a similar *ortho* coupling occurred in the pyrolysis experiments. Diphenylarsinic acid was unstable in the gaseous phase and shows the formation of anhydride and peroxide at the temperatures employed.

In a paper devoted to the ^{14}N NMR spectra of covalent azides, the data from a number of arsenic azides of the type R_2AsN_3, $RR'AsN_3$, $RAs(X)N_3$ (where X = halogen), and $(Ph_4As)_xM(N_3)_y$ (where M is a metal such as Sn, Pb, Au, Pt, or Pd) have been included [192]. Arsenic azides of the type R_2AsN_3 would be expected to exhibit three signals due to the three different nitrogen atoms in the molecule $>As-\overset{-}{N}_a-\overset{+}{N}_b{=}N_c$ and indeed such lines were seen but the lines due to N_a and N_c were invariably broader than those due to N_b and could not always be clearly seen. When run as neat liquids the ^{14}N NMR signals from Me_2AsN_3 and Et_2AsN_3 gave results which were interpreted as an indication of association of these compounds of the following type:



Tzschach and Kiesel [193] have extended our knowledge of arseno compounds $(C_6H_{11}As)_4$, (*tert*-BuAs)$_4$, (*sec*-BuAs)$_4$, (*iso*-BuAs)$_5$ and (*n*-BuAs)$_5$ by the reaction of the corresponding dichloroarsines with sodium. With the exception of the cyclohexyl compound, which was not sufficiently soluble in benzene, molecular weights were determined cryoscopically in benzene. The mass spectrum of the cyclohexyl compound gave a molecular ion $(C_6H_{11}As)_4^+$ with a relative intensity of 35%. Similarily the mass spectrum of the *tert*-Bu compound gave a molecular ion with relative intensity of 24%. The crystal structures of these two compounds were also determined.

The *tert*-Bu compound reacted with MeI in the following manner:

$$(tert\text{-}BuAs)_4 + 6MeI \rightarrow 2(tert\text{-}BuMe_3As)I + 2tert\text{-}BuAsI_2$$

Oxygen cleaved the As-C bond of the *tert*-Bu compound to give As_2O_3 but sulfur did not react. Both iodine and bromine also cleaved the As-C bond:

$$(tert\text{-}BuAs)_4 + 4I_2 \rightarrow 4tert\text{-}BuAsI_2$$

$$(tert\text{-}BuAs)_4 + 8Br_2 \rightarrow 4tert\text{-}BuBr + 4AsBr_3$$

With two equivalents of potassium metal the following reaction occurred in dioxane:

$$(tert\text{-}BuAs)_4 + 2K \xrightarrow{\text{dioxane}} KAs(tert\text{-}Bu)(As\text{-}tert\text{-}Bu)_2As(tert\text{-}Bu)K$$

This latter compound was isolated as a crystalline substance associated with 3 moles of dioxane. With excess potassium in THF the compound KAs(*tert*-Bu)As(*tert*-Bu)K·THF was obtained.

The preparation of a number of arsenicals containing As-Ge bonds has been described by Anderson and Drake [194]. Various methods were employed for the synthesis of these compounds. Thus Me_2AsGeH_3 and $Me_2AsGeMe_3$ were both obtained by the following reaction:

$$LiAl(AsMe_2)_3H + 4R_3GeBr \rightarrow 3R_3GeAsMe_2 + R_3GeH + LiBr + AlBr_3$$

(R = H or Me).

The best method for preparing many of the compounds involved exchange reactions with silylarsines:

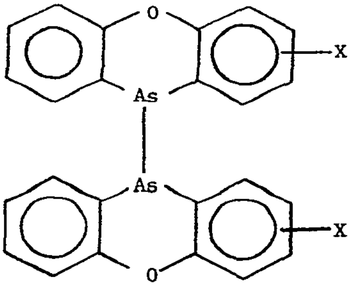
$$R'_2AsSiH_3 + R_3GeX \rightarrow R_3GeAsR'_2 + SiH_3X$$

(R' = Me or Ph, R = H or Me, X = F, Cl or Br).

In a short communication Zakharkin and Kyskin [195] have reported that the phospha- and arsacarboranes, p-$B_{10}H_{10}XCH$ (X = P or As), when treated witl sodium in the presence of naphthalene in THF solution, add two electrons to form the dianions $(p\text{-}B_{10}H_{10}XCH)^{2-}$. These dianions then rapidly rearrange to give the meta dianions $(m\text{-}B_{10}H_{10}XCH)^{2-}$ which can then be oxidized with $CuCl_2$ to the m-$B_{10}H_{10}XCH$ compounds. The action of Na and naphthalene on the *o*- and *m*-carbonanes proceeded in a complex manner.

ESR data for a variety of radicals obtained by γ-irradiation at 77°K of various compounds including triethylarsine have been reported by Lyons and coworkers [196]. The radical from triethylarsine appears to be $(Et_3As)_2^+$ but there appears to be a second radical which was tentatively assigned to rotating Et_4As radicals or to related Et_3AsR radicals. The unpaired electron for all of the radicals studied was in an antibonding σ orbital.

A U.S. patent [197] describes the preparation of halogenated diarines of the type XXVII for use as protective agents against marine fouling organisms.

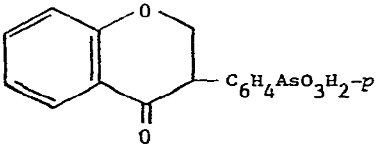


XXVII

where X = 2-Cl, 4-Cl, or H.

7. ARSONIC AND ARSINIC ACIDS

A number of arsonic acids have been obtained by coupling diazotized arsanilic acid with various chromanones, thiochromanones, 1-dioxides of thiochromanones and thiochroman-2,4-diones and subsequently decomposing these coupled products with the loss of nitrogen [198]. An example of the type of compound prepared is XXVIII.

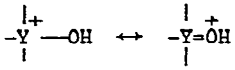


XXVIII

The compounds were tested against a virulent strain of *Entamoeba histolytica* and found to have very little activity.

Aryl-substituted esters of arsonic acids p-$XC_6H_4AsO(OR')_2$ (where X = H, Me, or NO_2 and R' = Ph or p-MeC_6H_4) were prepared by tranesterification of alkyl esters such as p-$XC_6H_4AsO(OEt)_2$ with phenol or p-cresol in the presence of acetic acid [199]. The alcohol liberated in the transesterification reaction was removed by continous distillation.

It is well known that the nitration of benzenearsonic acid is much more difficult than the nitration of phenylphosphonic acid, a fact which had been attributed to deactivation of the arsonic acid by protonation. Modro and Piekoś [200] have now made a thorough study of the nitration of these two acids as well as several closely related phosphorus compounds. The kinetics of the nitration reaction were obtained and the rate coefficients were plotted vs. the acidity of the nitration medium. On the basis of these results the authors concluded that both benzenearsonic and phenylphosphonic acids were protonated under the nitration conditions used and that the difference in reactivities between the arsonic and phosphonic acids was largely due to a lack of p_π-d_π interaction of the following type,



$$-\overset{|}{\underset{|}{Y}}{}^{+}-OH \leftrightarrow -\overset{|}{\underset{|}{Y}}=\overset{+}{O}H$$

(where Y = P or As)

in the case of the arsenic compound.

In continuation of previous work on electrophilic displacement of the arsono group in aromatic compounds containing powerful electron-releasing substituents Modro and coworkers [201] investigated the reaction of the so-called dioxane dibromide $C_4H_8O_2\cdot Br_2$ with 2-R-4-R'$C_6H_3AsO_3H_2$, where R = R' = OH, R = Me, R' = OH, and R = H, R' = OH. With the first compound only 4-bromoresorcinol was obtained but with the other two compounds a mixture of mono-, di- and tri-bromo derivatives was isolated.

A study of the loss in weight on heating of alkanearsonic acids $RAsO_3H_2$ where R = CH_3 through n-$C_{20}H_{41}$ has been made by Smith and coworkers [202]. Thermogravimetric analysis was used to obtain thermogravimetric curves as a function of temperature. The results indicated that pyroacids RAs(O)(OH)OAs(O)(OH)R were first formed which then lost water further to give polymeric anhydrides $(RAsO_2)_n$. On further heating these decomposed to give As_2O_3, alkanols, and gases which were not identified.

The IR spectra of butane-, hexane-, heptane-, octane-, and decanearsonic acids, as well as benzene-, *o*-toluene-, *p*-toluene-, *p*-ethylbenzene-, and *p*-biphenylarsonic acids have been reported by Dietze [203] and assignments of the various frequencies made. In the spectra of the alkanearsonic acids no band corresponding to an As-C mode could be distinguished, while in the arenearsonic acids the As-O frequencies were obscured by phenyl bands. The IR and Raman spectra of compounds of the type $Me_2MO(O)XMe_2$, where M was Al, Ga, or In and X was either P or As, have been measured, and assignments of the various bands have been made [204].

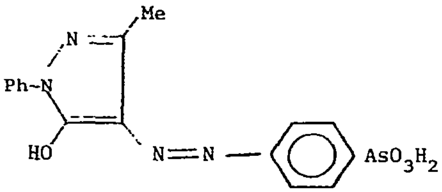
The IR and Raman spectra of the Li, Na, and K salts of $MeAsO_3H_2$ and the Na and K salts of $EtAsO_3H_2$ have been reported [205]. Several salts were in the hydrated form. It was concluded that there was no vibrational coupling between the alkyl group and the AsO_3 group and that the latter possessed C_{3V} symmetry. The IR spectra were determined as Nujol mulls or in KBr pellets while the Raman spectra were determined in aqueous solution. Simon and Schumann [206] have also reported on the Raman and IR spectra of the esters $MeAsO(OMe)_2$, $MeAsO(OEt)_2$, $EtAsO(OMe)_2$, and $EtAsO(OEt)_2$. They concluded that the $C\text{-}AsO(OC)_2$ skeleton probably possessed C_s symmetry.

Cobalt(II), nickel(II), zinc(II) and cadmium(II) salts of benzenearsonic and *o*-arsanilic acids were prepared by Sandhu and Sandhu [207] and their IR and reflectance spectra as well as paramagnetic susceptibilities determined. It was concluded that the cobalt and nickel compounds possessed distorted octahedral structures.

The preparation of metallic complexes of *o*-arsanilic acid with the metals Co, Ni, Cu, Zn and Cd has been described by Maslennikova and Shemyakin [208]. All complexes possessed the formula ML, where M was the metal and L the ligand, *o*-arsanilic acid. Some spectral properties of the complexes were listed.

The formation of red- or violet-colored products by the reaction of $AuCl_3$ and such arsonic acids as 2-amino-6-methyl-, 2-amino-5-methyl-, and 2-salicylideneamino-3,5-dimethylbenzenearsonic acids, has been the subject of a paper by Holzbecher and Volka [209]. The colored complexes were unstable and formed colored oxidation products and precipitated colloidal Au; the complexes were more stable when extracted into organic solvents. The compounds can be used for the determination of gold but possessed no advantage over *o*-arsanilic acid.

A new arsonic acid XXIX has been synthesized and used for the gradimetric determination of zirconium [210].

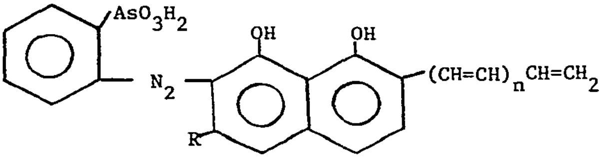


XXIX

The use of Arsenazo III for the determination of the antibiotic tetracycline in samples of blood has been reported by Alykova and Terent'ev [211].

A determination of the dissociation constants of Arsenazo M, a new reagent for the determination of rare earths, has been reported by Spitsyn and coworkers [212]. The dissociation constants were determined spectrophotometrically over a pH range between 0 and 13.5. Dissociation constants of Arsenazo M complexes of rare earths were also reported.

A paper on hypothetical models for polyene-Arsenazo I compounds of the type XXX suggests that cases where n = 6 or 7 should be good reagents for spectrophotometric analysis [213].



XXX

A method for the quantitative determination of arsenic in both inorganic and organic arsenic compounds on a micro scale has been advocated by Hassan and Eldesouky [214]. With organic arsenic compounds the organic matter was first destroyed by digestion with HNO_3-H_2O_2 for 15 min then by further digestion with perchlorie acid. Arsenic was then precipitated as $MgNH_4AsO_4$ with excess magnesia mixture, and excess magnesium was determined by atomic absorption spectrophotometry at 282.5 nm. The results with a number of different arenearsonic acids were excellent.

The use of benzenearsonic acid (as well as various other organometallic compounds) as catalysts in the preparation of polyamides is described in the patent literature [215].

A U.S. patent covers the preparation of arsenic containing bisazides for use as negative photoresists in the fabrication of microelectronics [216]. Two compounds mentioned were bis(*p*-azidophenyl)arsenic acid and *p*-arseno(*p*-azidobenzylidene)aniline.

8. TERTIARY ARSINE OXIDES AND RELATED COMPOUNDS

It is well known that the oxidation of enantiomeric tertiary arsines to the corresponding oxides in which H_2O_2, $KMnO_4$ or HNO_3 is used as the oxidizing agent, results in racemization due to the intermediate formation of the dihydroxides, $R_3As(OH)_2$. Gatilov and coworkers [217] have now introduced N_2O_4 as an oxidizing agent and demonstrated that the oxidation occurs with the formation of optically active arsine oxides with the same sign of rotation as the original arsine (but with increased optical activity). In the case of the oxidation of tertiary arsine sulfides with N_2O_4, however, the sign of rotation is reversed, which the authors attributed to partial racemization. The optically active arsine oxides racemized readily in solution.

On the basis of elementary analysis and IR spectra the structure of the products formed from tertiary arsine oxides and alkyl halides were believed to possess the structure $[R_3As(OH)O\overset{+}{As}R_3]X$; by contrast X-ray diffraction studies suggested the hydrogen-bonded structure $[R_3AsO{-}{-}{-}H^+{-}{-}{-}OAsR_3]X$. Shagidullin and coworkers [218] have further studied the IR spectra of several of these compounds such as $(Me_3AsO)_2HI$, $(Et_3AsO)_2HX$ (X = Cl, Br and I), $[(n\text{-}C_3H_7)_3AsO]_2HI$, and $(Ph_3AsO)_2HX$ (X = Br and ClO).

They concluded that the IR data was more in accordance with the symmetrical hydrogen bonded structure. In the case of $(Et_3AsO)_2HX$ in $CHCl_3$ or MeCN solution, however, there was some dissociation:

$$(Et_3AsO)_2HX \rightleftarrows Et_3AsO{\cdot}HX + Et_3AsO$$

The reaction of trialkylarsine oxides with alkyl halides was further extended by Chernokal'skii and Vorob'eva [219]. The reaction became more difficult with higher alkyl derivatives, and the authors were unable to prepare a crystalline product from *n*-Bu_3AsO and isobutyl iodide. The use of bromides and chlorides gave similar results to those obtained with iodides. The authors state that the following reaction must be fairly general:

$$2R_3AsO + XCR'_2CHR''_2 \rightarrow (R_3AsO)_2HX + R'_2C = CR''_2$$

In several cases, however, instead of the 2:1 adduct, a 1:1 adduct was obtained:

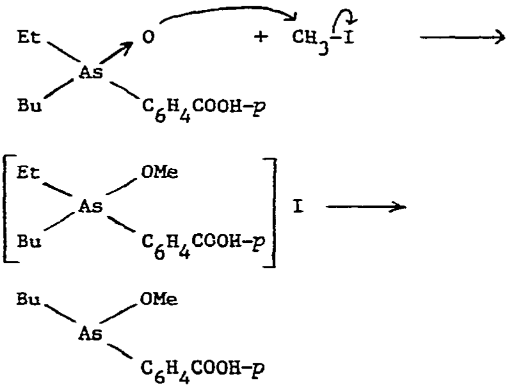
$$R_3AsO + R'I \rightarrow [R_3AsOH]I$$

With Et_3AsO and MeI both the 2:1 and the 1:1 adducts have been isolated. Both types of adducts have been synthesized independently from the arsine oxides and hydrogen iodide. In the case of Et_3AsO and isobutyl iodide, a compound having properties similar to isobutane was isolated from the reaction.

In contrast to the findings of Chernokal'skii and coworkers, Gatilov and Kralichkina [220] found that diethylphenylarsine oxide reacted with alkyl halides in a similar manner to trialkylarsine sulfides, *i.e.* with the formation of a quasiarsonium compound which then rearranged to give an ester of an arsinous acid:

$$PhEt_2AsO + RX \rightarrow [PhEt_2AsOR]X \xrightarrow{\Delta} PhEtAsOR + EtX$$

Gatilov and coworkers [221], who have contributed extensively to the literature on the stereochemistry of organoarsenicals, have now demonstrated that tertiary arsine oxides react with alkyl halides with the formation of esters of arsinous acids. For example butyl-*p*-carboxyphenylmethylarsine oxide reacted with methyl iodide in nitromethane solution at 30° to give methyl butyl-*p*-carboxyphenylarsinite with the intermediate formation of an arsonium salt:



The intermediate arsonium salt was formed rapidly and was actually isolated in 9.4% yield after the above reaction had run for 20 min. The reaction was followed both polarimetrically and by differential thermal analysis.

The integral intensities of the infrared absorptions of the As=O grouping in trialkyl- and triarylarsine oxides and arsonates were found to exceed those of the analagous P=O and C=O compounds [222]. The integral intensities of arsine oxides exceeded those for arsonates. In a closely related paper Shagidullin and Chernova [223] have compared the IR spectra of a series of *p*-substituted phenylphosphonates and *p*-substituted phenyldiethylarsine oxides. The P-O and As-O stretching frequencies in both sets of compounds correlated with the Hammett substituent constants, but no correlation with intensities of absorption could be found. From the IR and UV data the authors concluded that there was conjugation between the arsenic atom and the phenyl ring.

Saraswathi and Soundararaian [224], on the basis of IR spectral data, have reported that the hydrogen peroxide adducts of Ph_3PO and Ph_3AsO are simple 2:1 adducts held together by H bonds.

The capacity of the As=O grouping to form hydrogen bonds with suitable hydrogen donor molecules has been studied by Shagidullin and Avakumova [225]. They used phenol and the three As=O compounds, $(EtO)_3AsO$, $(EtO)_2$-PhAsO, and Et_2PhAsO, and concluded that the As=O grouping was more basic in compounds of the type R_3AsO compared with $(RO)_3AsO$.

The pK_a values for the conjugate acids of a series of six 10-phenyl-substituted 10-aryl-5,10-dihydrophenarsazine oxides as well as 10-phenyl-5,10-dihydrophenarsazine oxide itself have been reported [226]. A plot of Hammett σ constants vs. the pK_a values of the conjugate acids gave a straight line which conformed to the equation:

$$pK_a = 3.06 - 1.01\ \sigma$$

The pK_a values were obtained by potentiometric titration of the oxides with 0.1 N HCl in 4:1 ethanol-water at 25°. In another paper Kamai and coworkers [227] have appeared to refine their pK_a data for the same group of compounds. The resulting equation was

$$pK_a = -1.072\sigma^\circ - 0.249\sigma R^+ + 3.063.$$

The IR and Raman spectra of several oxides including Ph_3AsO have been recorded, and assignments of all of the observed frequencies were made [228] The spectra of complexes of the oxides with triphenylmethanol and with Me_3COD were also listed. The hydrogen bond had a marked effect on the vibrations of the OH or OD grouping.

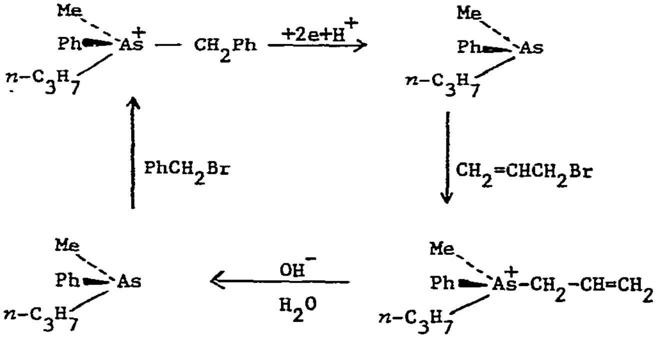
From IR and Raman spectral measurements the force constant for the As-O bond in Me_3AsO has been calculated to be 5.82 mdynes/A [229]. The donor strength of the arsine oxide towards MoO_2Cl_2 and $SbCl_5$ has also been investigated by way of IR and Raman spectroscopy.

In a paper from Sandhu's laboratory cobalt complexes containing the ligands $Ph_2As(O)CH_2CH_2As(O)Ph_2$ and $Ph_2As(O)(CH_2)_4As(O)Ph_2$, as well as the corresponding phosphorus compounds, have been described [230]. Molar con-conductance, magnetic susceptibility measurements at different temperatures, IR and reflectance spectral data were all used to determine the structures of the complexes.

The following papers have appeared in which tertiary arsine oxides have been used as ligands to the following metals: cobalt [62,231), copper [73], iron [86,232], manganese [233], nickel [234], tin [159], and uranium [235].

9. ARSONIUM COMPOUNDS AND ARSENIC YLIDS

In contrast to phosphonium salts, which undergo alkaline cleavage with the formation of phosphine oxides with inversion of configuration, the alkaline cleavage of arsonium salts leads to tertiary arsines with retention of configuration. This result was shown by the following reaction scheme [236]



Thus, the starting benzylmethylphenyl-*n*-propylarsonium salt gave a value, $[\alpha]_D^{20} = -14.3$ and the same salt obtained by quaternization of the arsine with benzyl bromide gave a value, $[\alpha]_D^{20} = -12.8$. Since the other steps in the reaction sequence are known to proceed with retention of configuration, the alkaline cleavage of the arsonium salt must also proceed with retention of configuration. Two different reaction pathways for the alkaline cleavage of arsonium salts, depending on the temperatures of the reaction, are proposed.

The different reactions of $(n\text{-Bu})_4NBF_4$, Ph_4PBF_4, and Ph_4AsBF_4 with $AlH_3\cdot NMe_3$ have been described in a paper by Ehemann and coworkers [237]. The three reactions are:

$$(n\text{-Bu})_4NBH_4 + AlH_3\cdot NMe_3 \rightarrow (n\text{-Bu})_4[BH_4\cdot AlH_3\cdot NMe_3]$$

$$Ph_4PBH_4 + 2AlH_3\cdot NMe_3 \rightarrow Ph_4PAlH_4 + AlH_2BH_4\cdot NMe_3 + NMe_3$$

$$Ph_4AsBH_4 + AlH_3\cdot NMe_3 \rightarrow Ph_3As + H_2AlBH_4\cdot NMe_3 + C_6H_6$$

The preparation of the compounds $n\text{-Bu}_4NAlH_4$, Ph_4PAlH_4 and Ph_4AsAlH_4 was also described.

The reaction of the tertiary arsines Et_3As and $n\text{-Pr}_3As$ with NH_2Cl, of Me_3As, Et_3As and $n\text{-Pr}_3As$ with Me_2NCl and of both 10-Me- and 10-chloro-9,10-dihydrophenarsazines with NH_2Cl led in all cases to the formation of aminoarsonium chlorides [238]. Chloramination of the phenarsazines illustrated that the preferred site for amination was the arsenic atom rather than the nitrogen atom.

Mikul'shina, Nesmeyanov, and Reutov [239] have studied the reaction of alkyllithium compounds with tetraphenylarsonium bromide. In contrast to phosphorus compounds where ylids are formed, the reaction with arsonium bromides is much more complex. Thus when an excess of benzyllithium was added to tetraphenylarsonium bromide and the mixture boiled for 1 hr Ph_2CH_2, $PhCH_2CH_2Ph$, and biphenyl were obtained. Triphenylarsine and benzene were obtained in 80% yield. The authors suggest the following mechanism:

$$Ph_4AsBr + PhCH_2Li \rightarrow Ph_4AsCH_2Ph$$

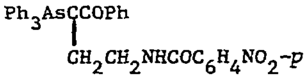
$$Ph_4AsCH_2Ph + PhCH_2Li \rightarrow Ph_3As(CH_2Ph)_2$$

$$Ph_3As(CH_2Ph)_2 \xrightarrow{\Delta} \text{products}$$

The decomposition, the authors suggest, can occur by both an intramolecular reaction and a free radical mechanism.

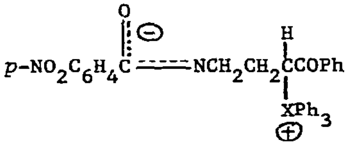
In addition to benzyllithium the authors have investigated the reaction of tetraphenylarsonium bromide with methyllithium and of benzyltriphenylarsonium iodide with *n*-butyllithium. In the first case the authors suggest that compounds such as Ph_4AsMe, Ph_3AsMe_2 and Ph_2AsMe_3 are formed which decompose by a free radical mechanism to give such products as CH_4, Me_3As, Me_2PhAs, $MePh_2As$, $(PhCH_2)_2$, biphenyl, benzene, Ph_2CH_2, and Ph_3As. With benzyltriphenylarsonium iodide and butyllithium the products of the reaction (after heating) included *trans*-stilbene and triphenylarsine which suggests that an ylid was formed. Other products suggest that there was also a second reaction pathway which involved the formation of butylbenzyltriphenylarsenic.

A comparison of the reaction of the As and P ylids, $Ph_3X = CHCOPh$, (X = P or As) with 1-*p*-nitrobenzoylaziridine has been made by Heine and Wachob [240]. The arsenic ylid reacts to form the new ylid XXXI, whereas the phosphorus ylid catalyzes the isomerization of the aziridine to form 2-*p*-nitrophenyl-2-oxazoline. A mechanism is proposed which involves nucleophilic attack of the carbanionic centers of either ylid on the aziridyl carbon to form similar intermediates XXXII, but a different pathway is then followed by the arsenic compound compared with the phosphous compound.



$$Ph_3As\underset{\displaystyle CH_2CH_2NHCOC_6H_4NO_2\text{-}p}{\underset{|}{C}}COPh$$

XXXI



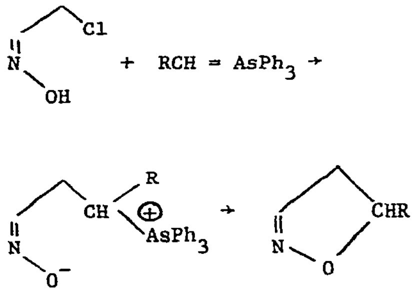
$$p\text{-}NO_2C_6H_4\overset{\overset{O}{\vdots}\;\ominus}{C}\text{-----}NCH_2CH_2\underset{\underset{\oplus}{XPh_3}}{\overset{H}{C}}COPh$$

(X = P or As)

XXXII

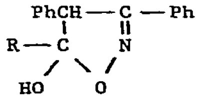
The reaction of stable arsenic ylids of the type $Ph_3As{=}CHCOR$ with ketones to give alkenes and triphenylarsine oxide was the subject of a paper by Nesmeyanov and coworkers [241]. The rate of reaction was considerably greater than in the case of phosphonium ylids. The reaction studied was that of cyclohexanone with the arsenic ylid $Ph_3As{=}CHCOR$ where R=OMe, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Ph, *p*-BrC_6H_4, and *m*-$NO_2C_6H_4$. The reaction of two ylids with acetone was also reported.

The preparation of Δ^2-isoxazolines by the reaction of keto-stabilized sulphonium or arsonium ylids with α-chlorooximes or the isomeric nitrosochlorides has been described by Bravo and coworkers [242]. The reaction involved is:



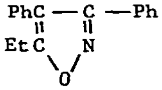
The arsenic ylids used were $MeCOCH{=}AsPh_3$, $PhCOCH{=}AsPh_3$, and *p*-$MeC_6H_4COCH = AsPh_3$.

In a paper largely devoted to the reactions of sulfonium ylids with α-nitrosoketones the reactions of three arsonium ylids, $CH_2{=}AsPh_3$, $MeCH{=}AsPh_3$, and $EtCH{=}AsPh_3$, with PhCOC(=NOH)Ph were studied [243]. The compounds formed were XXXIII and XXXIV:



R = H or Et

XXXXIII



XXXIV

In these reactions the arsonium ylids resembled the sulfonium ylids rather than the phosphonium ylids.

A study of pyridinium, triphenylphosphonium and triphenylarsonium 2,3,4-triphenylcyclopentadienylides has been made by Lloyd and Singer [244]. The phosphonium and arsonium ylids were air-stable yellow solids which were unaffected by alkali. They dissolved in dilute mineral acids and formed perchlorates with perchloric acid; protonation occurred at the 5-position. These ylids were more stable than the corresponding tetraphenylcyclopentadienylides, presumably due to less crowding. A number of reactions of the ylids were described, and their UV spectra were given.

In another paper Freeman, Lloyd, and Singer [245] have discussed the physical and chemical properties of the tetraphenylcyclopentadienylides of phosphorus, arsenic, antimony, and bismuth. The changes in properties as one descended the periodic table from phosphorus to bismuth were compared and the reactions of the ylids with aldehydes were also considered. This paper is discussed in considerable detail in the Antimony section.

The Raman and IR spectra, both in the solid state and in solution, of Ph_4AsI and $Ph_4AsNCO{\cdot}2H_2O$ have been reported by Ellestad and coworkers [246]. The observed frequencies for Ph_4As^+ were in agreement with those found by previous workers. Ellestad and coworkers [247] have also reported on the Raman and IR spectra of $Ph_4AsTeCN$.

In a paper devoted to the preparation and properties of a number of thioformates the compound $[Ph_4As][HCS_2]$ was described and its IR spectrum and crystal characteristics were given [248].

The preparation, IR and UV spectra, and X-ray data for the tetraphenylphosphonium and tetraphenylarsonium salts of the two anions $(CrO_3F)^-$ and $(CrO_3Cl)^-$ have been given [249]. The compound $(Ph_4As)(CrO_3Cl)$ is so insoluble in water that it may prove useful in the gravimetric determination of chromium.

Tetraphenylammonium, -phosphonium, -arsonium, and -stibonium salts of the anion $[Re_2Cl_8]^{2-}$ have been prepared and their IR spectra and magnetic susceptibilities determined [250]. The As-C stretching frequency in the tetraphenylarsonium cation was stated to occur at 460 cm^{-1}.

The ^{19}F and methyl ^{1}H NMR spectra as well as the IR CO stretching modes have been reported for the tetraphenylarsonium salts of the following tetrazole anions: $[Cr(CO)_5CF_3CN_4]$, $[Mo(CO)_5CF_3CN_4]$, $[W(CO)_5CF_3CN_4]$, $[Cr(CO)_5CH_3SCN_4]$, and $[W(CO)_5CH_3SCN_4]$ [251].

It is known that onium compounds act as catalysts for the liquid-phase oxidation of hydrocarbons such as cumene and α-pinene, and that the catalytic activity varies with the central atom of the onium compound as well as with substituents and with the anion. A molecular orbital study of this catalytic effect has been made by Ohkubo and Kanaeda [252) and among the onium compounds included was $[Me_4As]Cl$. The order of activity arsonium ≃ telluronium < selenonium was in accord with the AO populations of *d*-orbitals (in particular d_{xz} and d_{yz}) in these cations.

In a paper devoted to the nucleophicity of the cyanate ion Austad and coworkers [253] have compared the rate constants for the reactions:

$$Ph_4AsX + MeI \rightarrow Ph_4AsI + MeX$$

where X was CN^-, N_3^-, NCS^-, $NCSe^-$, NC^-, Cl^- and $MeCO_2^-$.

The rate constants for the reaction

$$Ph_3M + MeI \rightarrow Ph_3MeMI$$

(where M = As or P) were also given.

A short communication on the crystal structure of the compound $Ph_4As\cdot 2H_2O\cdot HCl_2$ [254] has shown that the molecule possesses the structure $[Ph_4As^+(H_2O\text{--}H\text{--}OH_2)^+]2Cl^-$, with the two water molecules being linked with a strong central hydrogen bond of length about 2.4 A.

A comparative study of Bu_4NBr and the tetraphenyl compounds Ph_4PCl,

Ph_4AsCl, and $NaBPh_4$ with regard to their partial molal volumes, heat capacities, and viscosities in water and in methanol solution has been made by Jolicoeur and coworkers [255]. It was concluded that there were sizeable differences in solute-solvent interactions between alkyl and aryl substituted ions.

Shirotani and coworkers [256] have reported on the anomalous electrical behavior of $[Ph_3MeP](TCNQ)_2$ and $[Ph_3MeAs](TCNQ)_2$ at high pressures.

The solubilities, degrees of dissociation, activity coefficients, and solubility products of tetraphenylphosphonium and tetraphenylarsonium picrates have been determined at 25° in mixtures of ethanol and water, varying between 100% ethanol and 100% water (by increments of 10%) [257].

Gibson and Weatherburn [258] have reported on the extraction of a number of quaternary phosphonium and arsonium salts into such organic solvents as $CHCl_3$, CH_2Cl_2, $(CH_2Cl)_2$, and $ClCH_2OCH_2Cl$ from aqueous salt solutions over a range of anion and cation concentrations. It was concluded that the quaternary salts existed as ion pairs or as dissociated ions in the organic phase. The results with $Ph_3MeAsCl$, however, were anomalous, and it was concluded that ion pairs were formed in the aqueous phase.

The use of Ph_4AsCl in the spectrophotometric determination of iridium has been reported [259].

A gravimetric method for the determination of gold which depends on the precipitation and weighing of $Ph_4AsAuCl_4$ has been proposed [260].

In connection with a study of transition metal compounds of pentachlorothiophenol, the arsonium salt $(Ph_4As)_2[Ni(SC_6Cl_5)_4]$ has been prepared and characterized by elemental analysis [261].

A number of papers have appeared in which ionic compounds were described where $[Ph_4As]^+$ or $[Ph_3MeAs]^+$ was the cation and the anion was a metal complex. Thus, such compounds as tetraphenylarsonium salts of $[Cr(NCO)_6]^-$ [262], $[PhPbX_4]^-$ (X = Cl or Br) [263], $[Ni(WOS_3)_2]^{2-}$, $[Co(WOS_3)_2]^{2-}$

and $[Zn(WOS_3)_2]^{2-}$ [264], $[HgCo_3(CO)_{12}]^-$ [265], $[UOCl_5]^{2-}$ [266], $[VO_2Cl_2]^-$ and $[VO_2F_2]^-$ [267] as well as methyltriphenylarsonium salts of $[Re_2(CO_7)I_3]^-$, $[Re(CO)_4I_2]^-$, and $[Re(CO)_3I_3]^-$ [268] have been described.

The use of triphenylallylarsonium bromide [269] and triphenylbenzylarsonium chloride [270] as corrosion inhibitors has been described.

An East German patent [271] describes the preparation of imido arsonium (as well as stibonium and bismuthonium) halides of the general type $[R_3AsNR'_2]X$, where NR'_2 is the succinimido or phthalimido group.

A Russian patent covers the preparation of higher tetraalkylarsonium hydroxides by treating the corresponding tetraalkylarsonium salts with 40% aqueous sodium hydroxide at an aqueous-organic phase boundary [272]. The organic phase is a 70:30 mixture of kerosine and isooctyl alcohol.

10. COMPOUNDS WITH As-S BONDS

Kuchen and coworkers [273] have described the UV and magnetic properties of a series of complex compounds obtained from dimethyldithioarsinic acid and a series of metals. The compounds studied were $(Me_2AsS_2)_2M$ (where M = Zn, Cd, Hg(II), Pb, Co(II), Ni(II)), $(Me_2AsS_2)_3In$, $(Me_2AsS_2)_3Cr$, Me_2AsS_2Tl, and $(Me_2AsS_2)_2Ni\cdot 2$ pyridine.

In continuation of previous work on the synthesis and properties of organoarsenicals, Gel'fond and coworkers [274] synthesized a number of diethylphenyl arsines with various substituents on the phenyl ring and converted these to the corresponding sulfides by reaction with sulfur in benzene. The oxidation of diethyl-*p*-tolyarsine with potassium permanganate led to the formation of diethyl-*p*-carboxyphenylarsine oxide which was reduced to the corresponding arsine with sulfur dioxide. Several compounds of the type $XC_6H_4As(S)(C_6H_5)_2$ were also reported.

An X-ray diffraction single crystal study of the compound $Ph_2As_2S_3$ has been made by Cordes and coworkers [275]. This compound was first prepared in 1882, but its structure had never been determined. The molecule is a five-membered non-planar ring with the sequence -As-S-As-S-S- and with one phenyl group attached to each arsenic atom.

In order to prepare organoarsenicals of the type R_2AsXR', where X was a chalcogen, O, S or Se, R an alkyl group, and R' an alkyl or aryl group, Sagan and coworkers [276] have investigated the reaction:

$$R_2AsNEt_2 + R'XH \rightarrow R_2AsXR' + Et_2NH$$

The preparation of Cl_2AsNEt_2 was readily accomplished starting with $AsCl_3$:

$$AsCl_3 + 2Et_2NH \rightarrow Cl_2AsNEt + Et_2NH_2Cl$$

A number of chalogen compounds were prepared, *e.g.* R_2AsOMe (R = Me, Et, and *n*-Pr), R_2AsSMe (R = Me and Et) and Me_2AsSeR' (R' = Ph, CH_2Ph, and 1-$C_{10}H_7$). The ^1H NMR data for the compounds prepared were listed as well as IR data.

The reaction of arsine sulfides of the type RR'_2AsS (where R and R' may be the same or different and R and R' are aromatic or aliphatic) with PCl_3 was investigated by Usacheva and Kamai [277]. With one exception compounds of the type RR'_2AsCl_2 were obtained. With triphenylarsine the reaction proceeded according to the equation:

$$Ph_3AsS + PCl_3 \rightarrow Ph_3As + PSCl_3$$

This result suggested that in all cases $PSCl_3$ was formed but except for triphenylarsine it reacted further to give the dichlorides. This conclusion was confirmed by showing that except for Ph_3As, the tertiary arsines reacted with $PSCl_3$ to give RR'_2AsCl_2.

The reaction of trivalent arsenic compounds which contain the As-S bond with alkyl halides has been studied by Chadaeva and coworkers [278]. In every case the As-S bond was broken with the formation of an arsenic halide:

$$R_2AsSR' + R''X \rightarrow R_2AsX + R'SR''$$

Similar results were obtained with compounds of the type $RAs(SR')_2$ and also in one case $(RS)_3As$. In the reaction of $Et_2AsSCOMe$ with MeI, $[Et_2MeAsI]I$ was isolated from the mixture.

The reaction of Grignard reagents with thioesters of trivalent arsenic acids occurred with complete cleavage of the As-S bond when these esters reacted with sufficient Grignard reagent [279]. Thus $(PhCH_2S)_3As$, $PhAs(SBu\text{-}n)_2$ and $EtPhAsSBu\text{-}n$ reacted with three, two and one mole of Grignard reagent, respectively, to give in each case the tertiary arsine:

$$(PhCH_2S)_3As + 3EtMgBr \rightarrow Et_3As$$

However, when lesser amounts of Grignard reagent were used thioesters were obtained:

$$(EtS)_3As + EtMgBr \rightarrow EtAs(SEt)_2$$

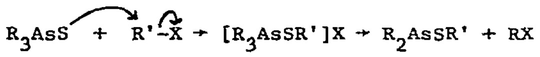
$$PhAs(SEt)_2 + EtMgBr \rightarrow EtPhAsSEt$$

Gatilov and coworkers have previously reported on the reaction between tertiary arsine sulfides and alkyl halides to form quasiarsonium salts which rearrange on heating to form thio esters of arsinous acids:

$$R_3AsS + R'X \rightarrow [R_3AsSR']X \xrightarrow{\Delta} R_2AsSR' + RX$$

The preparation of several of the arsonium salts and their rearrangement have now been reported [280]. The thio esters were also prepared independently for comparison with those obtained by the isomerization reaction.

In further work on this subject Gatilov and coworkers [281] reported on differential thermal analysis for the reaction:



$$R_3AsS + R'\text{-}X \rightarrow [R_3AsSR']X \rightarrow R_2AsSR' + RX$$

Because the quasiarsonium salts absorb moisture readily, with those salts which rearranged below 100° the thermogram showed two endotherms corresponding to the desorption of water and the transition to the ester. Salts which rearranged above 100° showed only the rearrangement peak.

The reactions of thioesters of trivalent arsenic acids with halogens and halogen-containing compounds have been reported by Chadaeva and coworkers [282]. Some of the reactions given are:

$$PhAs(SBu\text{-}n)_2 + Br_2 \rightarrow PhAsBr_2 + (n\text{-}BuS)_2$$

$$PhAs(SBu\text{-}n)_2 + 2PCl_5 \rightarrow PhAsCl_2 + 2PSCl_3 + 2n\text{-}BuCl$$

$$PhAs(SEt)_2 + SO_2Cl_2 \rightarrow PhAsCl_2 + (EtS)_2 + SO_2$$

$$PhAs(SEt)_2 + 2SO_2Cl_2 \rightarrow PhAsCl_2 + 2EtSCl + 2SO_2$$

$$PhAs(SBu\text{-}n) + 2HCl \rightarrow n\text{-}BuSH + PhAsCl_2 + (n\text{-}BuS)_2$$

$$Ph_2AsSPh + Br_2 \rightarrow Ph_2AsBr + PhSBr$$

$$2PhSBr \rightarrow Br_2 + (PhS)_2$$

$$Ph_2AsBr + Br_2 \rightarrow Ph_2AsBr_3$$

$$EtPhAsSEt + Br_2 \rightarrow EtPhAsBr + EtSBr$$

$$2EtSBr \rightarrow Br_2 + (EtS)_2$$

$$EtPhAsBr + Br_2 \rightarrow PhAsBr_2 + EtBr$$

$$EtPhAsSEt + EtPhPCl \rightarrow EtPhAsCl + EtPhPSEt$$

In a paper largely devoted to the reactions of $POCl_3$ and $PSCl_3$ with phosphines and with diphosphines, Lindner and Beer [283] showed that $Ph_2AsCH_2CH_2AsPh_2$ was oxidized with $PSCl_3$ to form $Ph_2As(S)CH_2CH_2As(S)Ph_2$ and PCl_3.

The diphenyldithioarsinato complexes of Ni(II), Co(II), Zn(II), In(III), Cr(III), and V(III) were prepared, and their UV and IR spectra were reported [284].

In a later paper [285] from this same laboratory the electronic absorption spectra of a number of ligands from both groups IVA and VA of the periodic system in association with such metals as V(III), Cr(III), Co(III), Rh(III), and Ir(III) have been studied. The arsenic-containing ligands were $Me_2AsS_2^-$ and $Ph_2AsS_2^-$. All of the ligands studied were of the type $R_nX(Y)Z^-$, where R was an alkyl or aryl group, X was a Group IV or VA element, and Y and Z were S or Se. The effects of all of these groupings, R, X, Y, and Z on the nephelauxetic parameter and the value of the bonding in the ligands was correlated.

The ESR spectrum of the arsenanyl radical, $As^{\cdot}X_4$, has been studied by Davies and coworkers [286]. The radical was obtained in solution by means of the following reactions:

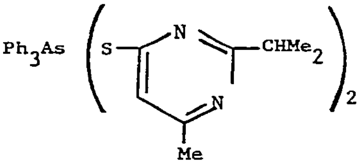
$$t\text{-BuSSBu-}t \xrightarrow{h\nu} 2t\text{-BuS}^{\cdot}$$

$$t\text{-BuS}^{\cdot} + AsMe_3 \rightarrow t\text{-BuSAs}^{\cdot}Me_3$$

Other disulfides or alkanethiols in the presence of Me_3As gave similar results. UV irradiation of a mixture of di-*t*-butyl peroxide and trimethylarsine in isopentane gave the ESR spectrum of the Me radical and a quartet whose spectrum was assigned to the radical $Me_2As(OBu\text{-}t)_2$.

The IR and Raman spectra of a series of alkyl and arylarsine sulfides of the type R_3AsS and Ar_3AsS have been determined by Shagidullin and coworkers [287]. All compounds had intense As-S bands between 460 and 500 cm^{-1} in both IR and Raman spectra. The frequency of the bands decreased as the electron-donating ability of substituents on the phenyl ring increased.

A fungicidal compound derived from pyrimidinethiols and triphenylarsine has been described in a South African patent [288]. The compound had the structure XXXV.

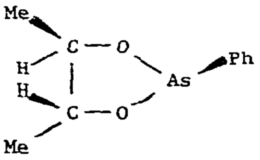


XXXV

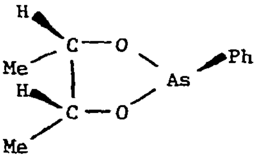
Copper(I) complexes of Ph_3AsS as well as a number of complexes of R_3PS and R_3PSe have been reported by Tiethof and coworkers [289]. The complexes have the general formula $(CuL_3)Y$, where L is the arsenic or phosphorus ligand and Y is ClO_4^- or BF_4^-.

11. MISCELLANEOUS

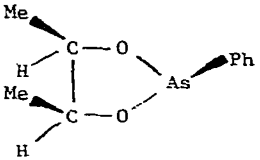
2-Phenyl-4,5-dimethyl-1,3,2-dioxaarsolane was prepared by the reaction of racemic 2,3-butanediol with $PhAsCl_2$ [290]. The compound should exist in one *trans* form (XXXVI) and two *cis* forms, *anti* (XXXVII) and *syn* (XXXVIII).



XXXVI



XXXVII

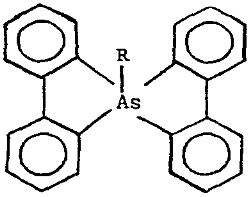


XXXVIII

The compounds XXXVII and XXXVIII are interconvertible by inversion at arsenic. The ^1H NMR spectrum of the reaction product indicated that 58% of the mixture existed in the *trans* form and 42% in the *cis* form. However, only one of the *cis* forms was present in any measurable amount. The authors were uncertain as to which of the two *cis* forms predonimated.

It is well known that pentaphenylantimony exists as a square pyramid in the solid state whereas pentaphenylarsenic is a trigonal bipyramid. The structure of these two compounds in solution has now been deduced from vibrational spectra and NMR spectroscopy and it is clear that the differences in geometry of the two compounds have been maintained in solution [291]. The paper is discussed in greater detail in the Antimony section.

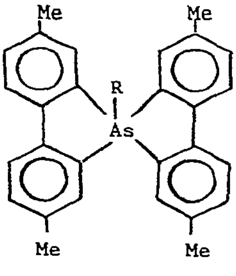
Hellwinkel and Knabe [292] in an interesting paper, report on the ^1H NMR spectra of several spirocyclic arsenicals. One group of compounds is shown as XXXIX.



a R = Et
b R = CH_2Ph
c R = $CHMe_2$

XXXIX

Since the arsenic atom should possess a trigonal bipyramidal structure and the two bridging biphenylene groups should each be equatorial and axially oriented, the molecule in the absence of ligand exchange would be chiral. Indeed the authors found, for example, that XXXIX c gave two doublets for the methyl group at -27° which coalesced at 35° and became a sharp doublet at 90°. Similarly, XXXIX b gave a doublet of doublets for the methylene protons at -50° and a single sharp signal at room temperature. In addition to XXXIX the authors also prepared and studied the ^1H NMR spectra of XL.



a R = CH_2Ph
b R = 2-biphenylyl

XL

Here the authors were able to observe not only the ^1H signal of the benzyl group (in XLa) as a doublet of doublets at low temperature which coalesced to a singlet at higher temperatures but also the signals due to axial and equatorial methyl groups which again coalesced as the temperature was raised.

The authors calculated $\Delta G^{\ddagger}$ values which varied from 12.3 to 15.4 kcal/mole for the ligand-exchange process. These values were only slightly lower (0.5 kcal/mole) than those of the corresponding phosphorus compounds. By contrast the antimony compounds gave $\Delta G^{\ddagger}$ values about 4 kcal/mole lower. These results were explained on a steric basis.

The preparation of ketoxime esters of the general type $PhAs(ON{=}CR_2)_2$ or $R'As(ON{=}CR_2)_2$ (where R' is an alkyl group) by several different methods has been reported by Miftakhova and coworkers [293]. A direct esterification has proved successful:

$$PhAsO + 2HON{=}CR_2 \rightarrow PhAs(ON{=}CR_2) + H_2O.$$

In one case transesterification was successful:

$$PhAs(OEt)_2 + 2HON{=}C(Me)Et \rightarrow PhAs[ON{=}C(Me)Et]_2 + 2EtOH.$$

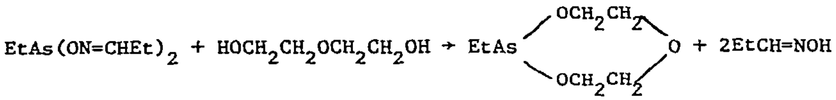
Finally the reaction of alkyl- or aryldichloroarsines with ketoximes in the presence of triethylamine was used successfully. Miftakhova and coworkers [294] have also prepared aldoxime esters of alkanearsonous and dialkylarsinous acids by the reaction of alkyldihaloarsines or dialkylhaloarsines with an aldoxime in the presence of triethylamine. They were also able to prepare an aldoxime ester by the following reaction:

$$(Et_2As)_2O + 2HON{=}CHMe \rightarrow 2Et_2AsON{=}CHMe + H_2O$$

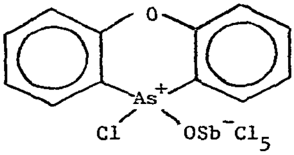
The aldoxime esters could be changed into other esters by transesterification:

$$BuAs(ON{=}CHC_3H_7\text{-}n)_2 + BuOH \rightarrow BuAs(OBu)ON{=}CHC_3H_7\text{-}n + n\text{-}C_3H_7CH{=}NOH.$$

From diethylene glycol a cyclic ester was obtained:



Holliday and coworkers [295] report on a single-crystal X-ray defraction study of the structure of the adduct formed from 10-phenoxarsine chloride (10-chloro-5,10-dihydrophenoxarsine) and $SbCl_5$. The compound has the structure XLI and is formed when the two compounds are refluxed without exclusion of atmospheric oxygen.



XLI

Bond distances and bond angles for the adduct are given. In a paper from this same laboratory the crystal structure of bis(5,10-dihydrophenoxarine) sulfide was reported [296]. The two phenoxarsine rings were nearly planar while the As-S-As angle was 99.87°. The dihedral angles at the two As----O lines of fold were 175.2° and 178.5°.

The new compounds $(p\text{-}Me_2NC_6H_4)_3AsX_2$, where X = Cl, Br, and I, as well as the related phosphorus and antimony compounds, plus $(p\text{-}Me_2NC_6H_4)_3SbF_2$ and $(p\text{-}Me_2NC_6H_4)_3BiCl_2$ have been prepared by Keck and Klar [297]. The authors report the ^1H NMR data for the *o*- and *m*-protons (in relation to the heteroatom) and report a straight-line correlation between the chemical shift of these protons and the electronegativity of the principal quantum number of the valence electrons of the heteroatom. This paper is discussed in greater detail under Antimony.

Keck and Klar [298] also report on the preparation of the interesting new type of arsenic and antimony cations $(p\text{-}Me_2NC_6H_4)_3As^{2+}$ and $(p\text{-}Me_2NC_6H_4)_3Sb^{2+}$

where the anion is $[SbCl_6]^-$. These compounds, which are dark blue in color, were prepared according to the reaction:

$$(p\text{-}Me_2NC_6H_4)_3AsCl_2 + 2SbCl_5 \rightarrow [(p\text{-}Me_2NC_6H_4)_3As][SbCl_6]_2$$

A comparison of the UV spectrum as well as the ^1H NMR of these compounds with the corresponding spectrum of the hexachloroantimonate salt of Crystal Violet indicated that these compounds probably possess a similar structure. The authors point out that these compounds are the first examples of heteroatoms with coordination number 3 and oxidation number of +5.

Stec and coworkers [299] have reported on chemical shifts in the binding energies of the electrons in 3p and 3d orbitals in a series of 32 arsenic compounds as measured by X-ray photoelectron spectroscopy. About an equal number of inorganic and organic arsenic compounds were included in the study. There was the expected increase in binding energy with an increase in the electronegativity of the substituents attached to arsenic.

ESR data for a number of radicals of the type $R_2C^{\cdot}CR_2m$, where R = H or an alkyl group and m is a metal or metalloid such as Sn, P, As, Si or Ge substituted with other alkyl groups [300]. For example the arsenic compounds employed were radicals derived from Et_3As, $HAsEt_3^+$, and Et_4AsI. It was found that hyperfine coupling to β-atoms in the carbon π-radicals was quite large, corresponding to as much as 6% delocalization into the heteroatom valence s orbital. It was also found that the radicals all have a preferred conformation in which the heteroatom is constrained above the radical plane, so that overlap between the carbon 2p orbital nominally containing the unpaired electron, and the carbon-heteroatom σ-bond is a maximum.

In another paper from Lyon's laboratory the ESR spectra of other radicals containing such elements as Si, Ge, Sn, Pb, P, and As were discussed [301]. Again the radicals were prepared by γ-radiation of the appropriate organic compound. The only arsenic compound used was $\mathrm{MeCH\overset{+}{As}Et_3}$ derived from tetraethylarsonium iodide. From the magnitudes of the hyperfine coupling to α-protons, methyl protons, and the heteroatom nuclei, it was concluded that for all of these radicals, delocalization into the heteroatom was small, $<\sim 1\%$.

It was originally proposed by Ingold and Roberts that reaction of tertiary arsines with oxy radicals involved the intermediate formation of a four-coordinate arsanyl radical:

$$\mathrm{RO^{\cdot} + R'_3As \rightarrow [RO\dot{A}sR'_3]}$$

Furimsky and coworkers [302] have now presented ESR evidence for the formation of this arsanyl radical during the photolysis of di-*tert*-butyl peroxide in the presence of triphenylarsine. In isopentane at -90° a four-line spectrum ($I=3/2$ for ^{75}As) was observed which was consistent with the radical *tert*-$\mathrm{BuO\dot{A}sPh_3}$. The radical was believed to decompose by α-scission:

$$\textit{tert}\text{-}\mathrm{BuO\dot{A}sPh_3} \rightarrow \textit{tert}\text{-}\mathrm{BuOAsPh_2} + \mathrm{\dot{P}h}$$

In continuation of previous work on the cleavage of the Si-P and Si-As bond with inorganic halides, Byrne and Russ [303] have reported on the reactions of $Me_3SiAsMe_2$ with $SiCl_4$, SiF_4, SO_2Cl_2, and SO_2F_2. With $SiCl_4$ and $Me_3SiAsMe_2$, Me_3SiCl and $Me_2AsSiCl_3$ were formed, but SiF_4 reacted only slightly even at 150° and 20 atmospheres. The reaction of SO_2Cl_2 with $Me_3SiAsMe_2$ was complicated and gave several different products; SO_2F_2 did not react with the arsenical.

Monomeric compounds with P-B, As-B, and Sb-B bonds have been prepared by Becker and Nöth [304]. Two arsenic compounds were described, namely $(Me_2N)_2BAsEt_2$ and $Et_2NB(AsEt_2)_2$. The compounds were prepared by reaction of the lithium derivative $LiAsEt_2$ with the appropriate dialkylaminoboron halide. The ^{11}B and ^{1}H NMR spectra were given and discussed in some detail.

The PMR spectra of methylmercury derivatives of *m*- and *p*-carbaphosphaborane and *m*- and *p*-arsacarboranes have been reported by Federov and coworkers [305]. The compounds were synthesized by the reaction:

$$m\text{- or } p\text{-}B_{10}H_{10}YCH \xrightarrow{RLi} m\text{- or } p\text{-}B_{10}H_{10}YCLi \xrightarrow{MeHgBr} m\text{- or } p\text{-}B_{10}H_{10}YCHHgMe$$

(where Y = P or As).

The *o*-compounds could not be synthesized by this method. The PMR spectra suggested that the electron-acceptor ability of the systems increased in the order $p\text{-}CHB_{10}H_{10}CH \leq p\text{-}AsB_{10}H_{10}CH < p\text{-}PB_{10}H_{10}CH$ and $m\text{-}CHB_{10}H_{10}CH < m\text{-}AsB_{10}H_{10}CH < m\text{-}PB_{10}H_{10}CH$.

The NQR spectra of ^{75}As in the three compounds 1-arsa-2-, 1-arsa-7-, and 1-arsa-12-carbalkosododecaboranes (*o*-, *m*-, and *p*-carbaarsaboranes) have been reported by Bryukhova and coworkers [306]. The distortion of the pyramid arising when one boron atom is replaced by a carbon atom causes a rather large increase in the NQR frequency of the ^{75}As for *o*-carbaarsaboran in comparison with the *m*- and *p*-isomers. It was also noted that the *o*-compound was least stable to the action of organolithium and organomagnesium compounds, which the authors believed was due to differences in electron distribution on the heteroatom in the *o*-isomer as compared with the *m*- and *p*-isomers, as is indicated also by the NQR results.

A method for the gasometric determination of the arsenate ion and of arylarsonic acids by reaction of these with phenylhydrazine in HCl solution and measurement of the nitrogen evolved has been suggested by Hassan [307]. The reaction was stated to be:

$$PhNHNH_2 + 2ArAsO_3H_2 \rightarrow PhOH + 2\ ArAsO + 3H_2O + N_2$$

With 2,4-difluorobenzenearsonic acid the accuracy was 99.8% but with *p*-hydroxybenzenearsonic acid only 81%.

A method for the determination of arsenic in biological materials has been suggested which depends upon the conversion of arsenic to triphenylarsine after drying and incinerating the biological material in a Schöniger flask [308]. Any arsenic present in the incinerated material was converted to a dithiocarbamate and was then heated with $MgPh_2$ solution and the resulting triphenylarsine was determined by gas chromatography.

A method for the determination of arsenic (and antimony) in organic compounds has been described by Bigois [309]. After destruction of organic matter by conventional wet digestion methods, the arsenic was oxidized to As(V). This was then titrated using iodine generated by constant-current electrolycis of KI, with $Na_2S_2O_3$ as an intermediate reagent. An amperometric end point was used and the iodine consumption was measured coulometrically.

Papers have appeared in which organoarsenic compounds have found biological use, either in antigen-antibody studies [310-312], as supplements [313-315] or contaminants [316] in feed for poultry or domestic animals, or as fungicides [288].

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