ARSENIC

ANNUAL SURVEY COVERING THE YEAR 1973

G. O. DOAK AND LEON D. FREEDMAN

*Department of Chemistry, North Carolina State University, Raleigh,
North Carolina 27607 (U.S.A.)*

TABLE OF CONTENTS

1. BOOKS AND REVIEWS

No books devoted solely to organoarsenic compounds have appeared in 1973. Organoarsenic compounds, however, have been mentioned in several books. The second volume of The Chemical Society's Specialist Periodical Reports on organometallic chemistry included a short section on organoarsenic, -antimony, and -bismuth compounds [1]. The use of tertiary arsines as donor molecules in coordination chemistry has been discussed in several books [2-4]. Those compounds subjected to X-ray analysis during 1971-1972 were listed in Volume 4 of *Molecular Structures and Dimensions* [5]. The mass spectrometry of organic arsenicals was also included in a book on mass spectrometry of inorganic and organometallic compounds [6]. A review article on covalent metal-carbon bonds gives the preparation and properties of organoarsenicals [7], while the electrochemistry of arsonium compounds is mentioned in another review article [8]. The use of organic arsenicals as ligands is discussed in a review article on binuclear complexes of transition elements [9]. Mislow [10] has reviewed work, largely from his laboratory, on the barriers to inversion in pyramidal phosphines and arsines.

2. PRIMARY AND SECONDARY ARSINES

Demuth and coworkers [11] have described the preparation and NMR spectra of $(CF_3)_2MD$ and CF_3MD_2, where M = P or As, from the corresponding iodo compounds, $(CF_3)_2MI$ and CF_3MI_2 and DI. The ^{19}F NMR spectra (and ^{31}P NMR spectra for phosphorus compounds) were then compared with those of the corresponding non-deuterated analogs. In each case there was a slight shift in the ^{19}F or ^{31}P spectra, varying from 0.09 to 0.18 ppm in the case of the ^{19}F NMR. The reason for these shifts was not apparent.

Two organoarsenic compounds containing the azido group have been described in a German patent [12]. The compound $(4\text{-}N_3C_6H_4)_2AsO_2H$ was prepared from $(4\text{-}NO_2C_6H_4)_2AsO_2H$ by reduction, diazotization of the resulting amino compound and treatment of the diazonium compound with NaN_3. The compound $4\text{-}N_3C_6H_4CH{=}NC_6H_4AsH_2\text{-}4$ was obtained from $4\text{-}H_2NC_6H_4AsH_2$ and $4\text{-}N_3C_6H_4CHO$.

Janzen and Viada [13] have studied the reaction of secondary phosphines and secondary arsines with hexafluoroacetone:

$$Ph_2MH + (CF_3)_2CO \rightarrow Ph_2MC(OH)(CF_3)_2$$

(where M = P or As)

The resulting phosphine was more susceptible to oxidation than the corresponding arsine. Oxidation of the phosphine with gaseous oxygen gave $Ph_2P(O)C(OH)(CF_3)_2$, whereas oxidation of the arsine under similar conditions gave $(Ph_2As)_2O$. The ^{19}F and ^1H NMR spectra of the arsenic compound were reported.

The IR spectra in the gas phase and the Raman spectra in the liquid phase have been determined for the molecules CF_3PH_2, CF_3PD_2, CF_3AsH_2, and CF_3AsD_2 by Bürger and coworkers [14]. With the exception of the torsional mode, all of the fundamental modes have been assigned. It was found that the degeneracy of the CF_3 vibrations were not removed by PH_2, PD_2, AsH_2 or AsD_2 groups. A normal coordinate analysis was made by the use of force constants previously obtained for HCF_3 and other XCF_3 derivatives. Gas phase IR and liquid phase Raman spectra of the compounds $(CF_3)_2PH$, $(CF_3)_2PD$, $(CF_3)_2AsH$, and $(CF_3)_2AsD$ were also recorded [15]. A normal coordinate analysis which made use of local symmetry force field for the CF_3 group as well as force constants from other CF_3 compounds was used for assigning the spectra.

3. TERTIARY ARSINES

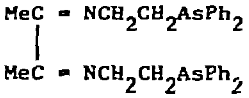
A Preparation

McAuliffe [16] has shown that the interesting arsenic compounds *o*-$Ph_2AsC_6H_4S(CH_2)_nSC_6H_4AsPh_2$-*o* react with nickel(II) salts with dealkylation of the methylene groups attached to sulfur. Thus the products were identicial with the product obtained by the reaction of *o*-mercaptophenyldiphenylarsine with the same nickel salts Three different arsenicals were used, *viz*. *o*-$Ph_2AsC_6H_4S(CH_2)_nSC_6H_4AsPh_2$-*o*, where n = 2, 3, or 4. The latter two compounds had apparently not been prepared previously.

The preparation of a number of new ligands containing the As-N bond and their use to form palladium complexes has been described by Morris and

Taylor [17]. The compounds $Ph_2AsCH_2CH_2NR_2$(R = H, Me, and Et) were characterized by elemental analyses and ^1H NMR spectra. The compounds $(Ph_2AsCH_2CH_2)_2NMe$ and $PhAs(CH_2CH_2NR_2)_2$ (R=H, Me or Et) could not be purified by distillation under reduced pressure. They were used for subsequent reactions without purification and were characterized only by their ^1H NMR spectra. Two other compounds were also obtained only in the crude state, $(Ph_2AsCH_2CH_2)NR$ (R=H or Et) but no spectral data were given. The compounds $PhAs(CH_2CH_2NR_2)_2$ (R=H, Me or Et) were prepared from $PhAsNa_2$ and the appropriate 2-chloroethylamine and details for their preparation were given. The compounds $(Ph_2AsCH_2CH_2)_2NR$ were prepared from $Ph_2AsK \cdot 2$ dioxane and the appropriate $(ClCH_2CH_2)_2NR$ but details of their preparation were not given. The compounds $Ph_2AsCH_2CH_2NR_2$(R=H, Me, or Et) were also prepared from $Ph_2AsK \cdot 2$ dioxane. Where R=H ethyleneimine was used; where R=Me or Et the appropriate dialkylaminoethyl chloride was used. Again details for their preparation were not given.

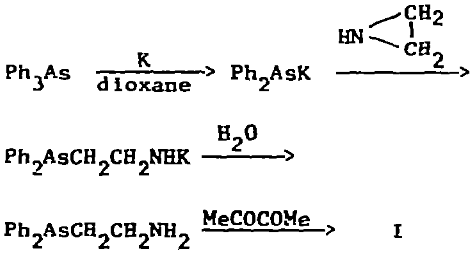
A new tetradentate ligand I has been synthesized, and its coordination compounds with nickel have been prepared and studied [18].



$$\begin{array}{l} MeC = NCH_2CH_2AsPh_2 \\ | \\ MeC = NCH_2CH_2AsPh_2 \end{array}$$

I

The following synthesis was employed to obtain the arsenic compound:



In an *Inorganic Syntheses* report [19] devoted to the preparation of diphosphines and mixed arsinophosphines, the preparation of 1-(dimethylphosphino)-3-(dimethylarsino)propane was described in detail:

$$Me_2PNa + ClCH_2CH_2CH_2AsMe_2 \rightarrow Me_2PCH_2CH_2CH_2AsMe_2 + NaCl$$

The preparation of *tert*-butyldi-*o*-tolylarsine and di-*tert*-butyl-*o*-tolylarsine from *o*-tolyllithium and *tert*-butyldichloroarsine or di-*tert*-butylchloroarsine, respectively, has been discribed by Shaw and Stainbank [20]. The compounds were characterized by their ^1H NMR spectra but not by elemental analyses. A number of coordination compounds of these two compounds with platinum were described.

A series of acetylenic arsenic compounds of the type $R_2AsC{\equiv}CR'$, where R was an alkyl group and R' was H, an alkyl, or other group, has been prepared by Kuz'min and coworkers [21]. The compounds $R_2AsC{\equiv}CH$ underwent normal Mannich, Favorski and Grignard reactions while oxidative condensation by CuCl and oxygen gave $R_2AsC{\equiv}CAsR_2$.

The reaction of sodium diphenylarsenide (from Ph_3As and Na in liquid NH_3) with chloroalkanoic acids yields the corresponding carboxy-substituted tertiary arsines [22]:

$$Ph_2AsNa + Cl(CH_2)_nCO_2Na \xrightarrow[H^+]{H_2O} Ph_2As(CH_2)_nCOOH$$

The chloroacids used were chloroacetic, α- and β-chloropropionic and α-, β-, and γ-chlorobutyric acids. The pKa values for the three acids $Ph_2As(CH_2)_nCOOH$ were n=1, 5.95; n=2, 6.02; n=3, 6.16. In an analogous way the amide $Ph_2AsCH_2CONH_2$ and the ester $Ph_2AsCH_2CO_2Et$ were prepared. The acid $Ph_2AsCH_2CO_2H$ was also converted to the acid chloride by treatment with $SOCl_2$, and this acid chloride gave the same amide or ester by treatment with ammonia or ethanol. The two acids $Ph_2As(CH_2)_nCOOH$, n = 2 or 3 reacted further with sodium in liquid NH_3 to give the sodium arsenides which with water gave $PhAs(H)(CH_2)_nCOOH$ (n = 2 or 3). In the case of $Ph_2AsCH_2CO_2H$ and $CH_3CH(AsPh_2)COOH$ the reaction with sodium in liquid ammonia resulted in cleavage of the aliphatic side chain:

$$Ph_2AsCH(R)CO_2H \xrightarrow[NH_3]{Na} Ph_2AsNa + NaCH(R)CO_2Na$$

$$(R = H \text{ or } Me)$$

Oxidation of the carboxy-substituted tertiary arsines by air, H_2O_2 or HgO gave the corresponding arsine oxides.

A general method for preparing chiral tertiary arsines has been published by Stackhouse, Cook, and Mislow [23]. The method depends upon the synthesis of menthyl methylphenylarsinite from *l*-menthol and methylphenyliodioarsine. This material was then sulfurized to yield *l*-menthyl methylphenylthioarsinate. This can then be separated into its two diastereomeric forms by fractional crystallization The CD curve of the two isomers was enantiomeric in type and the absolute configurations were assigned from the ^1H NMR spectrun on the basis of previous work with menthyl phenylphosphonates. Reaction of either diastereomer of *l*-menthyl methylphenylthioarsinate with either alkyl- or aryllithium reagents led to cleavage of both the As-S and As-O bonds and the formation of an optically pure tertiary arsine. This latter reaction proceeded with inversion of configuration at the arsenic atom. Displacement of menthoxide was shown to proceed with some racemization but there was no loss of specificity in the desulfurization step. The authors prepared methylphenyl-*n*-propylarsine $[\alpha]_D$ + 10.7 and methylphenyl-2-naphthylarsine $[\alpha]_D$ + 1.7 by means of this new synthesis.

In continuation of earlier work on the resolution of chiral tertiary arsines Gatilou and Yambushev [24] prepared *p*-[ethyl-*o*-bromophenylarsino]-benzoic acid by oxidation of ethyl-*o*-bromophenyl-*p*-tolylarsine with potassium permanganate followed by reduction of the resulting arsine oxide. The arsine was resolved by the use of quinine and the resulting enantiomeric arsines were converted to the optically active arsine oxides or arsine sulfides by oxidation with NO_2 or S, respectively.

Gatilov and coworkers [25] have synthesized three isomeric tertiary arsines containing amino-substituted phenyl groups:

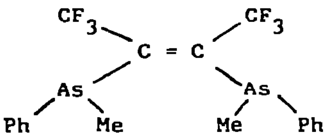
$$Et(p\text{-}MeC_6H_4)AsCl + 2Na + BrC_6H_4NH_2 \rightarrow Et(p\text{-}MeC_6H_4)AsC_6H_4NH_2 + 2NaCl$$

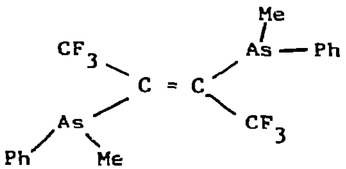
The three isomeric *o*-, *m*-, and *p*-bromoanilines were used in the above reactions and in addition to the tertiary arsines the coupling products $[Et(p\text{-}MeC_6H_4)As]_2$ and $H_2NC_6H_4C_6H_4NH_2$ were obtained. The tertiary arsines were isolated as dark red liquids which were not readily distilled. They formed crystalline salts with HCl, HNO_3 and H_2SO_4 but not with organic acids such as acetic, propionic or malic. Limited IR data on the arsines were given.

The reaction of arsenic(III) fluoride with tetrafluoroethylene in the presence of antimony(V) fluoride led to the formation of $(C_2F_5)_3As$ and $(C_2F_5)_2AsF$ which were separated by distillation [26]. The reaction was carried out in an autoclave at 260 psi. No analyses or characterizations of the compounds were given.

Bis(pentafluoroethyl)fluoroarsine and tris(pentafluoroethyl)arsine were also prpared in 42.3 and 26% yields, respectively, from tetrafluoroethylene and AsF_3 at atmospheric pressure [27]. From $(C_2F_5)_2AsF$ a number of derivatives were prepared. Thus from the corresponding alkali halides $(C_2F_5)_2AsCl$, $(C_2F_5)_2AsBr$ and $(C_2F_5)_2AsI$ were obtained. Ethanol, in the presence of SiO_2 to absorb HF, gave $(C_2F_5)_2AsOEt$, while diethylamine gave $(C_2F_5)_2AsNEt_2$. Reaction with PhMgBr gave $(C_2F_5)_2AsPh$. Hydrolysis gave $[(C_2F_5)_2As]_2O$. Arsenic analyses and mass spectra were used to characterize the compounds.

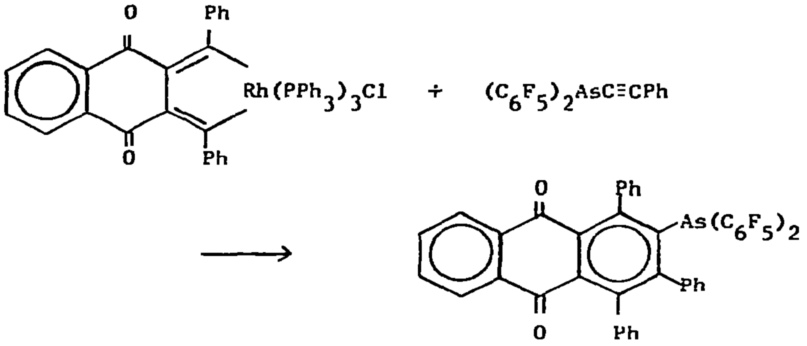
Cullen and Mihichuk [28] have described the reaction of 1,2-dimethyl-1,2-diphenyldiarsine with hexafluoro-2-butyne to form an approximately 1:1 mixture of *cis*- and *trans*-2,3-bis(methylphenylarsino)-hexafluoro-2-butene:





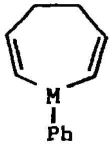
If, however, hexafluoroacetone was used as the solvent, the *cis* form predominated. Since there are two assymetric arsenic atoms the *cis* form was separated into the two diastereomeric *meso* and *dl* forms. A study was then carried out on the reactions of the diastereoisomers with $Fe(CO)_5$. From the results it was possible to assign configurations to the starting ligands.

In a paper on the reaction of the heterocyclic rhodium complex II with acetylene derivatives the following reaction was discussed [29]:



The $(C_6F_5)_2AsC{\equiv}CPh$ was prepared from $PhC{\equiv}CMgBr$ and $(C_6F_5)_2AsCl$. The reaction of the rhodium complex with P, S, and Se acetylenic compounds was also discussed.

The preparation of both 1-phenyl-4,5-dihydrophosphepin (III, M = P) and 1-phenyl-4,5-dihydroarsepin (III, M = As) by the cycloaddition of phenylphosphine or phenylarsine to hexa-1,5-diyne has been described by Märkl and Dannhardt [30].

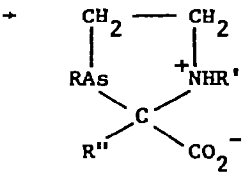


III

The compounds were characterized by IR, ^1H NMR, and mass spectrometry. Both compounds were readily quaternized with alkyl halides (MeI and $C_6H_5CH_2Br$ for the arsenic compound) and were also converted to the corresponding oxides by oxidation.

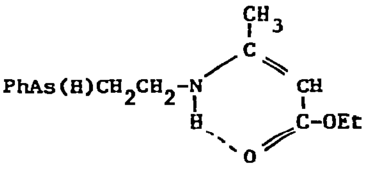
Tzschach and Heinicke [31] have described the preparation of a series of 1,3-azarsolidine carboxylic acids by the condensation of (2-aminoethyl)-arsines with α-ketoacids:

$$RAs(H)CH_2CH_2NHR' + R''COCO_2H$$

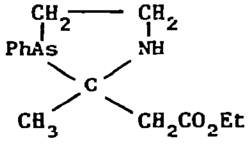


where R = Ph, R' = H or Et, and R'' = Me
R = Ph, R' = H, and R'' = Ph
R = C_6H_{11}, R' = H or Et, and R'' = Me
R = *n*-Bu, R' = H, and R'' = Me

In addition to the above carboxylic acids several 1,3-azarsolidine carboxylic esters were prepared from $MeCOCO_2Et$ and $PhCOCO_2Et$. The reaction of $PhAs(H)CH_2CH_2NH_2$ with ethyl acetoacetate gave either of two products depending on the acidity or alkalinity of the reaction medium. In neutral or alkaline solution IV was obtained, but in acid solution V was the product.

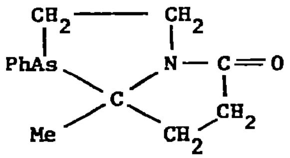


IV

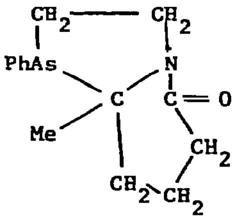


V

Both levulinic and γ-acetylbutyric acid reacted with $PhAs(H)CH_2CH_2NH_2$ to give VI and VII, respectively.

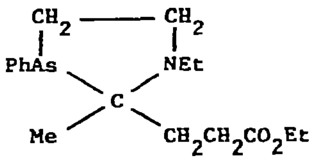


VI



VII

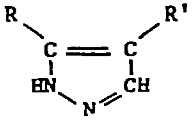
Ethyl levulinate reacted to give VIII.



VIII

IR data for some of the compounds were given.

In a study devoted to the 1,3-dipolar cycloaddition of diazomethane to alkynes to form pyrazoles, arsenicals of the type IX were formed [32].



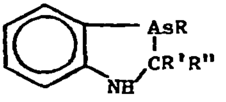
IX

where R = Ph_2As, R' = H or CO_2Me, and

R = $Ph_2As(O)$, R' = H

The pyrazoles were identified by means of their ^1H NMR spectra, and it was shown that the cycloaddition pathway was governed more by steric than by electronic effects. Pyrazoles containing other heteroatoms such as Sn, Pb, Si, Ge, and S were also prepared by this method.

The synthesis of a series of 1,3-benzazarsolines (X) by the reaction between *o*-aminophenylarsines *o*-$C_6H_4(NH_2)AsH_2$ or *o*-$C_6H_4(NH_2)AsHR$ and aldehydes, ketones or ketoesters has been described by Tzschach, Drohne, and Heinicke [33].

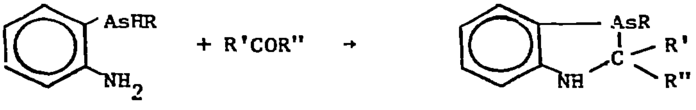


X

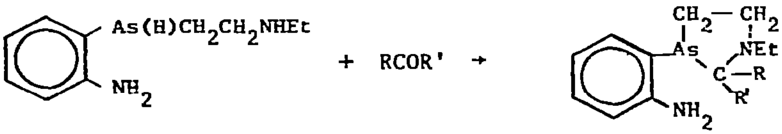
(Where R = H or alkyl, R' = H, Ph or alkyl, and

R" = alkyl, Ph, CO_2Et or CH_2CO_2Et).

o-Aminophenylarsine was prepared by the reduction of *o*-nitrophenylarsonic acid. It forms a monosodium arsenide when treated with sodium in liquid ammonia, which can then be converted to the secondary arsine *o*-C_6H_4AsHR by treatment with an alkyl halide, where R = Et, *i*-pr, *n*-Bu or C_2H_4NHEt. The aminoarsines then reacted with aldehydes, ketones of ketoesters as follows:

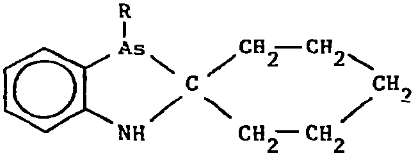


The aminoarsine *o*-$NH_2C_6H_4As(H)CH_2CH_2NHEt$ reacted with benzaldelyde or with acetone as follows:



(where R = Ph, R' = H, R = R' = Me)

From *o*-$NH_2C_6H_4AsH_2$ and cyclohexanone the spirocyclic compound XI (R=H) was prepared.



XI

When XI (R=H) was treated with *n*-butyllithium in ether and the resulting lithium arsenide treated with EtI the compound XI (R=Et) was obtained.

A series of 10-aryl-substituted phenoxarsines have been prepared from 10-chlorophenoxarsine and the necessary aryl Grignard reagents [34].

Trimethylarsine was produced from Me_2AsO_2H, $MeAsO_3H_2$, sodium arsenate, or sodium arsenite when these compounds were incubated with three different fungi isolated from sewage [35].

A U.S. patent which covers the preparation of enamines and amidinium salts containing tertiary arsines has been issued [36]. The compound $\{[(Me_2N)_2C^+CH_2]_2AsPh\}2Cl^-$ was obtained from $PhAsCl_2$ and $CH_2 = C(NMe_2)_2$.

B. Spectra

The IR and Raman spectra as well as the ^{19}F NMR spectra of the three compounds $M(C{\equiv}CCF_3)_3$, where M = P, As, and Sb were determined [37]. The vibrational spectra were in agreement with C_{3v} symmetry for all three compounds. There was no evidence for hindered rotation of the CF_3 groups at room temperature as judged by the NMR spectra. The synthesis of the compounds and their mass spectra will be published in a separate paper.

By using the pure isotopes ^{58}Ni ^{62}Ni ^{54}Fe, and ^{57}Fe, metal complexes of these isotopes were prepared on a milligram scale with the ligand *o*-phenylene-bis(dimethylarsine) [38]. By comparing the far IR spectra of these complexes it was possible to assign the As-Ni and As-Fe stretching bands for these complexes. By comparison of these results with similar complexes of Co, Pt, and Pd, the Co-As, Pt-As and Pd-As stretching bands were also assigned. These bands are very weak and lie in the 325-295 cm^{-1} region for the Ni, Fe, and Co complexes and in the 270-210 cm^{-1} region for the Pt and Pd complexes.

The gas phase IR spectra and the Raman liquid spectra of the two compounds $(CF_3)_2PP(CF_3)_2$ and $(CF_3)_2AsAs(CF_3)_2$ have been determined [39]. The results were best interpreted in terms of *trans* conformations (C_{2h} symmetry) No evidence for any other rotamers for either compound was adduced. A normal coordinate analysis was also made by the use of force constants obtained from CF_3H, $(CF_3)_3M$ and $(CF_3)_2MH$, where M = P or As.

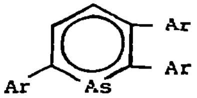
In a paper largely devoted to organophosphorus compounds, the use of IR spectroscopy for the determination of the amount of *p*- and π-complexing between phenol and such compounds as Ph_3N, Ph_3P, Ph_3As and Ph_3Sb were described [40].

In a paper largely devoted to antimony compounds and discussed in greater detail under Antimony, Brill and coworkers [41] have reported on the NQR spectra of the two arsines $(Ph_2As)_2CH_2$ and *p*-$C_6H_4(Ph_2AsCH_2)_2$. The spectra were not markedly different from the NQR spectra of Ph_3As and *p*-substituted triarylarsines which suggested that the CH_2-As bond was similar to the As-phenyl bond.

The NQR spectra for ^{75}As for the compounds $(C_2F_5)_3As$, $(CF_3CHF)_3As$, $(C_2F_5)_2AsF$ and $(C_2F_5)_2AsBr$ have been reported by Bryukhova and Kopaevich [42]. The ^{79}Br and ^{81}Br values for the last compound were also given. In agreement with their previous results with As(III) and Sb(III) compounds, it was concluded that asymmetry in the molecule led to an increase in the quadrupole constants of the central atom. The authors concluded that there was considerable distortion of the trigonal pyramid in unsymmetrically substituted compounds.

The mass spectra of the phosphorus and arsenic compounds *cis*- and *trans*- $Ph_2PCH{=}CHPPh_2$, *cis*- and *trans*- $Ph_2AsCH{=}CHAsPh_2$, *cis*- and *trans*- $Ph_2PCH{=}CHAsPh_2$, and $Pb_2PCH_2CH_2AsPh_2$ have been determined and their fragmentation patterns have been elucidated [43]. The *cis* and *trans* isomers were found to have identical mass spectra which suggested that there was free rotation about the C=C bond in the parent ions. It was also shown that phenyl migration occurred from one P to another P, or from one As to another As, but in the mixed P-As compounds phenyl migration from arsenic to phosphorus occurred but not the converse.

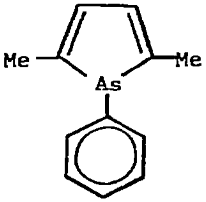
The crystal structure of the heterocyclic arsenic compound 2,3,6-triphenylarsenin (XII) has been determined [44].



XII

It was found that the arsenin ring did not differ significantly from C_{2v} symmetry. The ring is planar with a As-C distance of 1.872A, which is significantly less than the sum of the covalent radii (1.98A). A comparison was made between the arsenin ring and the related phosphorin ring.

In a paper from Märkl's laboratory [45] the photoelectron spectra of three 1-phenylphospholes and one arsole XIII were given. The results showed



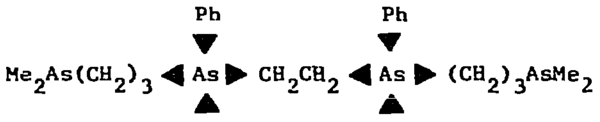
XIII

that there was no conjugative interaction between the five and six membered rings and that the lone pairs on phosphorus and probably on arsenic took no part in five-membered ring conjugation. The authors concluded that phospholes and arsoles in their ground state conformation consist of localized diene systems and lone pairs of hetero atom electrons and in this sense are not aromatic.

p-Nitrophenyldiethylarsine, its oxide and sulfide, *p*-nitrobenzenearsonic acid, and *m*-nitrophenyldiethylarsine and its sulfide were prepared in order to study the polarography of these compounds [46]. The reductions were carried out in DMF and gave two waves, a one-electron and a three-electron wave. It was concluded that in the second step products were formed which are oxidized at similar potentials and that only the NO_2 group undergoes the reduction. ESR spectra for the anion-radicals were studied and showed no delocalization of the odd electron into the aryl or alkyl substituents on the arsenic.

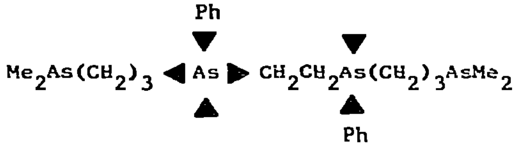
C. Use as Ligands

Bosnich and coworkers [47] have described the synthesis of the ligand $[Me_2As(CH_2)_3AsPhCH_2]_2$, which they named tetars. This compound should exist in *dl* and *meso* forms as follows:



$Me_2As(CH_2)_3\overset{Ph}{As}CH_2CH_2\overset{Ph}{As}(CH_2)_3AsMe_2$

meso

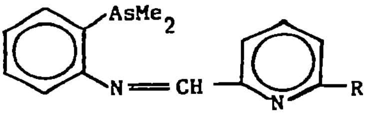


$Me_2As(CH_2)_3\overset{Ph}{As}CH_2CH_2\underset{Ph}{As}(CH_2)_3AsMe_2$

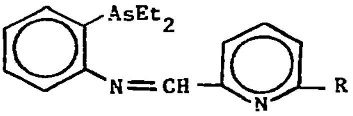
racemic

The racemic ligand formed complexes with cobalt stereospecifically because of the steric constraints of the two chiral arsenic centers. With $CoCl_2 \cdot 6H_2O$ the racemic ligand forms three different isomers *cis*-α, *cis*-β, and *trans*, whereas the *meso* ligand formed *cis*-β and *trans*. It was possible to separate all five complexes and to identify these by means of their ^1H NMR spectra. The various complexes were found to be in equilibrium and the racemic ligand did not show any strong topological preferences, whereas the *meso* ligand preferred the *trans* topology. By the use of benzoyl-(+)-tartaric acid monohydrate it was possible to resolve the *cis*-α complex of the racemic ligand and to obtain the pure enantiomers. Because the three compounds of the optically active ligand, *cis*-α, *cis*-β, and *trans* are in equilibrium, it was also found possible to convert the optically pure *cis*-α complex into optically active *cis*-β and *trans* complexes. By treating the cobalt complexes with NaCN, the optically active free arsine ligands were obtained. Thus from the pure *cis*-α$[Co(R,R\text{-tetars})Cl_2]Cl$ the optically pure S,S-tetars,[α] + 28.7,was isolated. A solution of R,S-tetars R,R;S,S-tetars (racemic), or S,S-tetars, when treated in methanol-ether solution with a few drops of HCl, isomerized and racemized rapidly to a mixture of 55% R,S-tetars and 45% R,R;S,S-tetars. The use of circular dichroism in helping to analyse the different isomers of the cobalt complexes is described in considerable detail.

The Schiff base condensation of *o*-dimethylarsino- or *o*-diethylarsinoanilines with the appropriate aldehyde led to the formation of the following new tridentate ligands [48]:

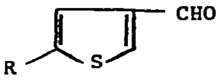


R = H or Me



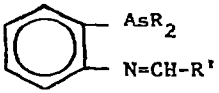
R = H or Et

The formation of a number of manganese(II) complexes of these ligands was studied, and their magnetic properties were given. In a second paper Chiswell and Lee [49] reported the formation of a number of cobalt and nickel complexes of several new ligands obtained by the condensation of *o*-dimethylarsino- and *o*-diethylarsinoanilines with the sulfur-containing aldehydes *o*-$MeSC_6H_4CHO$ and XIV. The new ligands were not characterized.



XIV (R = H or Me)

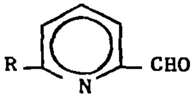
The preparation of four new ligands containing the tertiary arsine grouping and their complexes with cobalt or nickel has also been described by Chiswell and Lee [50]. The ligands all contained the grouping XV. They were obtained only as oils by condensation of the *o*-$R_2AsC_6H_4NH_2$ compound with an aldehyde and were not characterized.



XV

(R = Me or Et, R' = o-$Me_2NC_6H_4$
R = Me, R' = o-$HMeNC_6H_4$
R = Me, R' = 2-pyridyl)

In two later papers these same authors have described cobalt [51] and nickel [52] complexes of a number of new arsenic ligands obtained by the condensation of o-dimethylarsino- and o-diethylarsinoanilines with aldehydes (XVI).



XVI (R = H or Me)

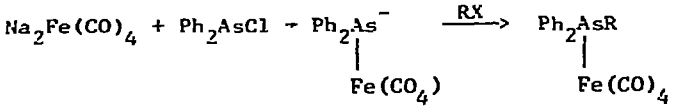
Again the new arsenic ligands were not characterized.

The reaction of a number of tertiary arsines with the iridium compound *trans*-Ir(CO)ClPPh$_3$ (Vaska's compound) to displace the PPh$_3$ and form new iridium compounds has been described by Chow and coworkers [53]. Among the arsenicals used were $Ph_2AsCH_2CH_2AsPh_2$, *cis*-Ph_2AsCH=$CHAsPh_2$, *cis*-Ph_2AsCH=$CHPPh_2$, and $Ph_2AsCH_2CH_2PPh_2$, but not all of the compounds reacted with Vaska's compound. Since Vaska's compound has the interesting property of reversibly binding an oxygen molecule, reaction of the new iridium compounds were studied as oxygen binders, and two of the compounds were shown to form stable irreversible oxygen adducts.

Fitzgerald and coworkers [54] have prepared several phosphine and arsine iridium complexes of the type $IrClCO(AsPh_3)_2$, $IrClCO(PPh_3)_2$, and $IrClCS(PPh_3)_2$ and studied their reactions with a variety of Lewis acids. On the basis of these results it was concluded that the order of basicity of the above compounds was in the order

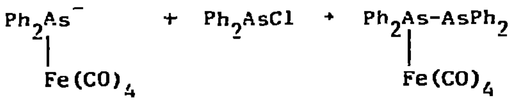
$$IrClCO(AsPh_3)_2 > IrClCO(PPh_3)_2 > IrClCS(PPh_3)_2$$

In continuation of studies on the use of $Na_2Fe(CO)_4$ in organic syntheses, Collman and coworkers [55] studied the reaction between this iron compound and diphenylchlorophosphine and -arsine. An anionic complex was formed which reacted further with various organic halides to form neutral phosphine and arsine complexes:



$$Na_2Fe(CO)_4 + Ph_2AsCl \rightarrow \underset{Fe(CO_4)}{\underset{|}{Ph_2As^-}} \xrightarrow{RX} \underset{Fe(CO)_4}{\underset{|}{Ph_2AsR}}$$

In the above reaction R was an organic group such as benzyl or an organometallic group such as Ph_3Ge. The anionic complex also reacted with Ph_2AsCl or Ph_2PCl to form compounds with As-As or As-P bonds:



$$\underset{Fe(CO)_4}{\underset{|}{Ph_2As^-}} + Ph_2AsCl \rightarrow \underset{Fe(CO)_4}{\underset{|}{Ph_2As}}\text{-}AsPh_2$$

The IR and ^{31}P NMR spectra of these compounds were briefly mentioned.

The ^1H NMR spectra of a series of coordination compounds formed between Et_3As as the donor molecule and Me_3Ga, Et_3Ga, Me_2GaCl and Et_2GaCl as acceptor molecules, have been reported and analysed [56]. The substitution of Cl for an alkyl group on the gallium atom increased the difference in chemical shift between the CH_3 and CH_2 moities of the ethyl group on the arsenic atom, from which it was concluded that the strength of the Ga-As bond was greater for the hologenated compound. From measurements of the complex formation constant with temperature, the bond energies of the Ga-As bond in three compounds was estimated.

The synthesis of compounds containing the Ga-As bond derived from Et_3As and such gallium compounds as Me_3Ga, Et_3Ga, and Et_2GaCl has also been described in another Russian paper [57].

In addition to the publications discussed above, a large number of other papers have described the use of tertiary arsines as ligands. The metals coordinated to the arsenic in the complexes included chromium [58-60], cobalt [61-66], copper [67,68], gold [69,70], iridium [67,71-74], iron [65, 67,75-81], manganese [67,82-88], mercury [89,90], molybdenum [59,67,91-99], nickel [100-103], osmium [67,104-107], palladium [67,89,108-112], platinum [67,89,108-110,112-119], rhenium [120-122], rhodium [71,72,123-128], ruthenium [67,105,129-135], silver [67,136], tin [137], titanium [137], and tungsten [59,91-93,138-140].

D. Other Chemical and Physical Properties

The potentiometric titration of a series of compounds of the type p-$Me_2NC_6H_4X$, where X was a substituent such as H, F, Me, NO, Cl, Br, etc., gave pKa values which were used to obtain a Hammett plot using the known σ values for the substituents [141]. In addition the two substituents p-Et_2As and p-Ph_2As were used and σ-values for these substituents were obtained. In addition pKa values for 10-[p-dimethylamino)phenyl]-5,10-dihydrophenarsazine and its arsine oxide were obtained and it was concluded that the phenarsazine ring system acted as an electron acceptor in respect to election distribution in its structure.

Splitter and Calvin [42] have calculated a Hammett ρ value of 2·5 for the inversion rate of a series of p-substituted 1-phenyl-2,2-dimethylaziridines. This ρ value was determined from experimental $\Delta G^{\ddagger}$ values adjusted to 25° by assuming $\Delta S^{\ddagger} = 0$. The resulting ρ value was then used to calculate σ_{inv} constants for a number of other substituents. Having determined these σ_{inv} constants, the authors then used these values to obtain ρ values for other 1-substituted aziridines, oxaziridines, acyclic amines, phosphines, and arsines. The ρ values for acyclic amines, phosphines, and arsines were in the ratio 0.5 : 1.0 : 1.25.

In a paper [143] on the reaction of Ph_3P, Ph_3As, and Ph_3Sb with $CuCl_2$, it is stated that the reaction rate, both in Me_2CO and MeOH, is in the order $Ph_3As < Ph_3P < Ph_3Sb$. The products of the reaction between Ph_3As and $CuCl_2$ were, however, not given.

Calculation of the electronic configuration of Ph_3M, where M = P, As, Sb, and Bi, has been reported in the Russian literature [144].

Two papers devoted to the electronic structures of heterocyclic organophosphorus and organoarsenic compounds have described the use of the CNDO/2 approach. In the first of these papers [145] several substituted phospholes and arsoles as well as phosphole and arsole were considered. Orbital energies and sequence, orbital density, total density plots and substituent effects were given and comparisons were made between arsoles, phospholes and pyrroles.

In the second paper [146] similar calculations were made for arsenic and the results compared with phosphorin and pyridine.

In a paper devoted to physical constants of gallium and arsenic compounds, the m.p. and enthalpy of melting of triethylarsine was given as 181.8°K and 2643 cal/mole, respectively [147]. In a closely related paper, the enthalpy of mixing of Et_3Ga and Pr_3Ga with Et_3As was given as -6.2 and -9.6 kcal/mole, respectively [148].

4. AMINOARSINES

A number of bis(dialkylamino)arsines of the type $MeAs(NR_2)_2$ have been prepared by Kober [149] by means of the reaction:

$$MeAsI_2 + 4R_2NH \rightarrow MeAs(NR_2)_2 + 2[R_2NH_2]I$$

All of the aminoarsines were liquids which were purified by distillation *in vacuo*. ^1H NMR, IR, and mass spectra of the products were reported. The As-N bond was cleaved by acids, water, alcohols, and sulfhydryl compounds:

$$MeAs(NR_2)_2 + 4HX \rightarrow MeAsX_2 + 2[R_2NH_2]X$$

$$Me_2AsNR_2 + R'OH \rightarrow Me_2AsOR' + R_2NH$$

The As-N bond also underwent exchange reactions with other amines:

$$MeAs(NMe_2)_2 + 2C_4H_4NH \rightarrow MeAs(NC_4H_4)_2 + 2Me_2NH$$

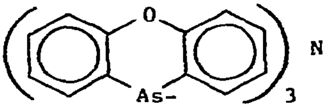
(where C_4H_4NH = pyrrole)

Kober [150] has found that Me_2AsNMe_2 undergoes transamination when treated with an excess of a secondary amine. Dimethylamine was evolved in the reaction and a number of new aminoarsines were prepared by this reaction. The reaction temperatures varied from 130 to 190°, and the yields varied from 40 to 60%. PMR and IR data were reported for the new aminoarsines

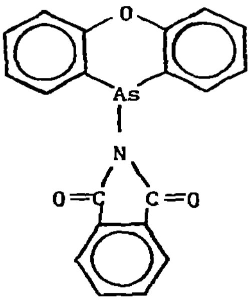
The reaction of primary amines with either Me_2AsCl or Me_2AsI led to the formation of bis(dimethylarsino)amines in yields of 40-60% [151]. The reactions were carried out in ether at -60 to -70°, and the products purified by vacuum distillation. The amines RNH_2 were R = Me, Et, *n*-Pr, *n*-Bu, iso-Bu, *sec*-Bu and *tert*-Bu. In the case of *tert*-$BuNH_2$ the compound $Me_2AsNHCMe_3$ was obtained. By the reaction of Me_2AsNMe_2 with aniline or cyclohexylamine $(Me_2As)_2NPh$ and $(Me_2As)_2NC_6H_{11}$ were obtained. The reaction of the arsinoamines with a wide variety of reagents was investigated. In all cases the AsN bond was cleaved. Thus with HX(X = F, Cl, Br, or I) Me_2AsX was obtained, with MeI, Me_2AsI was obtained and with R'OH, Me_2AsOR' was isolated. With AsF_3, Me_2AsF and a high-boiling oil were obtained. The ^1H NMR, IR, and mass spectra of the bis(dimethylarsino)amines were given.

A number of compounds containing ^{15}N-P bonds and a few compounds containing ^{15}N-As, ^{15}N-Si, and ^{15}N-B bonds have been prepared and the ^{15}N-^1H NMR coupling constants were determined in order to assess the importance of $N \rightarrow P\pi$ bonding in the phosphorus compounds [152]. The arsenic compounds synthesized were $(CF_3)_2As^{15}NH_2$ and $[(CF_3)_2As]_2{}^{15}NH$. The percent *s* character of the nitrogen was calculated from the ^{15}N-H coupling constants by means of the equation $s = 0.43J_{^{15}N\text{-}H} - 6$. The replacement of P by As resulted in a decrease in the percent of 2*s* character at nitrogen. By consideration of the Si-^{15}N and B-^{15}N compounds it was concluded that the equation giving the percent of *s* character was not applicable to organonitrogen-heteroatom compounds in which the electronegativity of the heteroatom differed markedly from that of carbon. The results were explained, therefore, by considering the redistribution of electrons within the σ frameworks of the molecules. It was further concluded that it was unnecessary to invoke $p_\pi - d_\pi$ bonding between the nitrogen and the heteroatom to explain the NMR results.

The reaction of 10-chlorophenoxarsine with NH_3 in xylene gave tris(10-phenoxarsinyl)amine(XVII) [153]. With potassium phthalimide the same phenoxarsine gave 10-N-phthalimidylphenoxarsine (XVIII).



XVII



XVIII

The reaction of the 10-chlorophenoxarsine with a series of sodium phenolates gave the corresponding 10-phenoxy compounds.

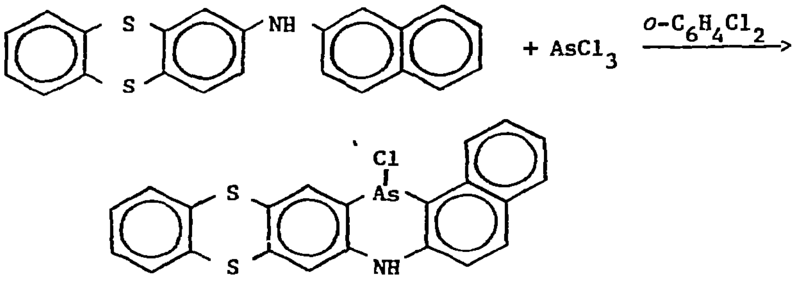
In a long and involved paper Krannich and coworkers [154] have reported on the reaction of several chloroarsines, the two diarsines $(Me_2As)_2$ and $(Ph_2As)_2$, as well as Ph_2AsCl_3, with ammonia and with ammonia-chloramine mixtures. With Me_2AsCl and ammonia the product was $[Me_2AsNH_3]Cl$ but with an ammonia-chloramine mixture the product had the composition $Me_4As_2N_2\cdot HCl$ whose structure was uncertain. A compound of similar composition was obtained from Et_2AsCl and ammonia-chloramine mixtures. In addition, Et_2AsCl gave an appreciable amount of the compound $(Et_2As)_3N$. Tetramethyldiarsine also reacted with ammonia-chloramine to give $Me_4As_2N_2\cdot HCl$. It was postulated that the methyl compound was a dimethylarsenonitrile hydrochloride tetramer but that the ethyl compound was a polymer with As-N and As-Cl bonds. Diphenylchloroarsine was found to react with ammonia-chloramine to give triclinic crystals of the product $(Ph_2AsN)_3$. The structure of this compound was established by three-dimensional X-ray analysis. Prolonged heating of the trimer in acetonitrile solution gave some crystals of the tetramer $(Ph_2AsN)_4$ whose structure was also determined by X-ray analysis. The reaction of Ph_2AsCl_3 with ammonia in a stainless steel bomb also produced the trimer $(Ph_2AsN)_3$. The structures of the various compounds given in this study were elucidated by means of mass spectral data as well as the above-mentioned X-ray data.

5. HALOARSINES

In a long paper devoted to the ^1H, ^{19}F and ^{13}C NMR spectra of an extensive series of polyfluoroalkyl arsines Kopaevich and coworkers [155] have analysed the effect of structure on the ^{19}F spectra of arsenic compounds of the type $(CF_3CF_2)_2AsX$, $(CF_3CF_2)_2AsR$ (where R was an alkyl or aryl group), $(CF_3CFCl)_2AsX$, and R_3As where R was a fluorine-substituted alkyl group. In compounds of the type $(CF_3CF_2)_2AsX$ the ^{19}F nuclei of the CF_2 groups are diastereotopic but the effect was evident, as judged by ^{19}F spectra, only where X = Br or I. In the compounds $(CF_3CF_2)_2AsCF(CF_3)X_1$ where a double type of diastereotopy might be expected, only the nonequivalence of the CF_3CF_2 groups was observed, while in $(CF_3CF_2)_2AsCF(CF_3)Cl$ no nonequivalence of fluorine containing groups was observed. The compounds $(CF_3CFCl)_2AsX$ possess two chiral and one prochiral centers which are observed in the ^{19}F spectra. It was also concluded on the basis of the NMR results that inversion at the As atom was relatively slow on the NMR time scale.

In continuation of their work on polyfluoroalkylarsines Kopaevich and coworkers [156] heated CF_2=CFCl with AsF_3 in a steel bomb with SbF_3 as a catalyst and obtained, after fractional distillation of the reaction product, $(CF_3CFCl)_2AsF$ (58%) and $(CF_3CFCl)_2AsCl$ (14%). The products were characterized by elemental analysis and mass spectrometry. In a similar reaction $(CF_3CF_2)_2AsF$ was found to react with $CF_2{=}CFCl$ to yield $(CF_3CF_2)_2AsCFClCF_3$ (70%) and $(CF_3CF_2)_2AsCF_2CF_2Cl$ (30%). A hydrolysis reaction (erronously termed a haloform reaction) was used to help determine their structure. The hydrolysis of the reaction mixture obtained from $(CF_3CF_2)_2AsF$ and $CF_2{=}CFCl$ with Et_3N in MeOH gave CF_3CF_2H, CF_3CHFCl, and $CF_2{=}CF_2$ in quantitative yields. The molar ratios of the products CF_3CHFCl and $CF_2{=}CF_2$ corresponded to the molar ratios of the isomeric arsines obtained in the reaction and also to the integrated intensities of the two products in their ^{19}F NMR spectra. The reaction of Et_3N in MeOH with $(CF_3CF_2)_3As$ led quantitatively to CF_3CF_2H; the same reaction with $(CF_3CFCl)_2AsF$ gave CF_3CFClH, also in quantitative yield. It was concluded that the $CF_2{=}CF_2$ arose by β-elimination of HCl from the $ClCF_2CF_2H$ which was formed by the hydrolysis of the $As{-}CF_2CF_2Cl$ grouping, in the compound $(CF_3CF_2)_2AsCF_2CF_2Cl$.

In a paper devoted to the chemistry of thianthrene the phenarsazine XIX was prepared by the following reaction [157]:

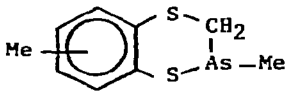


XIX

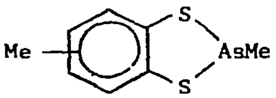
The yield was 20% and no spectral properties were given.

The reaction of $AsCl_3$ and diazomethane to form $MeAs(CH_2Cl)_2$ and $MeAs(Cl)CH_2Cl$, with the latter as the principal product, has been reported by Wieber and Eichhorn [158]. The reaction of $MeAs(Cl)CH_2Cl$ with a variety of nucleophiles in the presence of Et_3N was studied. With phenol $MeAs(OPh)_2$

was obtained while thiophenol gave a mixture of $MeAs(SPh)CH_2Cl$ and $MeAs(SPh)_2$. With $3,4\text{-}(SH)_2C_6H_3CH_3$ the two heterocyclic compounds XX and XXI were obtained in which the orientation of the CH_3 group was uncertain.



XX



XXI

Both IR and Raman spectra for the compounds $(C_6H_5\text{-}CH_2)_3MX_2$, where M = As or Sb and X = F or Cl have been reported [159]. Both ^1H and ^{19}F NMR spectra were also given. The vibrational spectra were interpreted in terms of a slightly-distorted trigonal bipyramid. The methylene NMR signal, which was split into a triplet by coupling with the two fluorine atoms in the compounds $(C_6H_5CH_2)_3SbF_2$ and $(C_6H_5CH_2)_3AsF_2$, but in the case of the antimony compound there was some collapse of the triplet which was interpreted as due to intermolecular exchange of the fluorine atoms.

In a paper largely devoted to phosphorus compounds, Moedritzer [160] has reported on the redistribution equilibria in the systems $MePBr_2$ vs. $MePCl_2$, $MePOCl_2$ vs. $MePO(OPh)_2$, $MePSBr_2$ vs. $MePSCl_2$, $MePSCl_2$ vs. $MePS(NMe_2)_2$ and $MeAsBr_2$ vs. $MeAsI_2$. The equilibria studied were

$$2\ MePXY \rightleftharpoons MePX_2 + MePY_2$$

$$2\ MeAsClI \rightleftharpoons MeAsCl_2 + MeAsI_2$$

Equilibrium constants were obtained for the phosphorus compounds. The method used depended upon the ^1H NMR signals obtained, and constants were obtained at various temperatures. With the arsenic compounds, however, the equilibrium was much faster than in the case of the phosphorus compounds both room temperature and -53°. Only a single sharp line with no evidence of fine structure was obtained.

The use of Me_2AsCl as a ligand has been reported by Ehrl and coworkers

[161]. Thus Me_2AsCl reacted with $C_7H_8Cr(CO)_4$ and $C_7H_8Mo(CO)_4$, where C_7H_8 was norbornadiene, to form the complexes *cis*-$(CO)_4Cr(AsMe_2Cl)_2$ and *cis*-$(CO)_4Mo(Me_2AsCl)_2$. The chromium complex reacted with $NaMn(CO)_5$ to form *cis*-$(CO)_4Cr[Me_2As{-}Mn(CO)_5]_2$. This latter compound was converted into its *trans*-isomer by refluxing in toluene for one hour. An attempt to prepare the corresponding molybdenum complex was unsuccessful.

6. OTHER TRIVALENT ARSENIC COMPOUNDS

Continuing their work on As and P compounds containing CF_3 groups, Demuth and Grobe [162] have described the preparation as well as the mass spectra and ^1H, ^{19}F, and ^{31}P NMR spectra of a series of compounds containing $P{-}PH_2$ and $As{-}PH_2$ bonds. The only arsenic compound obtained was $(CF_3)_2AsPH_2$, prepared by the following reaction:

$$Et_3SiPH_2 + (CF_3)_2AsI \rightarrow Et_3SiI + (CF_3)_2AsPH_2$$

The reaction of $(CF_3)_2AsI$ with $LiAs(PH_2)_4$ was less satisfactory.

In another paper from the same laboratory [163] the preparation of compounds of the type $Me_3MP(CF_3)_2$ and $Me_3MAs(CF_3)_2$ where M = Si, Ge, and Sn. The arsenic compound $Me_3SiAs(CF_3)_2$ was prepared by the following reaction:

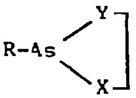
$$Me_3SiPH_2 + HAs(CF_3)_2 \rightarrow Me_3SiAs(CF_3)_2 + PH_3$$

The reaction was carried out for 30 days. In a similar manner from Me_3GePH_2 and Me_3SnPH_2 the compounds $Me_3GeAs(CF_3)_2$ and $Me_3SnAs(CF_3)_2$ were obtained. The IR spectra of the silicon and germanium compounds were listed and assignments of bands were made. The ^1H and ^{19}F NMR spectra were given and coupling constants were calculated.

The next paper of the series [164] was devoted to reactions of compounds of the type $(CF_3)_2PPH_2$ and $(CF_3)_2AsPH_2$ in which the P-P or As-P bond was cleaved. These bonds were cleaved by reaction with a variety of polar substances [HBr, $(CF_3)_2PI$, $(CF_3)_2AsI$, Me_3SnH, $(CF_3)_2AsH$] as well as by non-polar substances such as Br_2 and $Mn_2(CO)_{10}$. In addition exchange reactions were carried out with $(CF_3)_4P_2$, $(CF_3)_4As_2$, and P_2F_4. Among the arsenic compounds obtained in this manner were $(CF_3)_2AsPF_2$, and $(CF_3)_2PAs(CF_3)_2$. The reaction of P_2F_4 and $(CF_3)_2AsPH_2$ led to the compound $(CF_3)_2AsPF_2$. The ^1H and ^{19}F spectra were used extensively in characterization of the products.

Two interesting new compounds $CF_3P(PH_2)_2$ and $CF_3As(PH_2)_2$ have been prepared by the reaction of CF_3PI_2 or CF_3AsI_2 with H_3SiPH_2 at -22° [165]. The compounds were characterized by ^1H and ^{19}F NMR spectroscopy. No elemental analyses were given.

Aksnes and Vikane [166] have reported on the ^1H NMR spectra of a series of 1,3,2-dioxaarsolanes, 1,3,2-dithiarsolanes and one 1,3,2-oxathiarsolane:



R = Ph, X = Y = O, X = Y = S

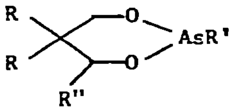
R = Cl, X = Y = O, X = Y = S

X = O, Y = S

R = Me, X = Y = O, X = Y = S.

A detailed analysis of the NMR spectrum of three of the compounds as AA'BB' systems and one as an ABCD system determined that the rings existed in a slightly distorted envelope conformation with the ring carbon adjacent to the O or S at the apex of the flap. There were apparently rapidly interconverting envelope conformations.

The use of NMR spectra for determining conformations of a series of substituted 1,3,2-dioxaarsenanes of the general formula XXII has been described by Samitov and coworkers [167].



XXII

In these compounds R' was Cl, OMe, OPh, or Ph. It was concluded that the ring existed in the chair conformation.

The ^{14}N NMR spectra of a series of alkyl-element azides, where the element was B, Al, Tl, C, Si, Ge, Sn, Pb, and As were determined [168]. The only arsenic compound studied was Me_2AsN_3, and the chemical shifts and line widths at half the peak height for this compound were given. It was concluded that the arsenic compound was a purely covalent azide.

The IR spectra of $[(CF_3)_2As]_2$ in both the gaseous and the solid state and the Raman spectra in the liquid and solid states were determined by Thompson and coworkers [169]. As an aid to interpreting the data these authors also determined the IR spectra of $(CF_3)_3As$ in the solid and gaseous states and the Raman spectrum in the liquid state. Assignments for the various vibrational bands for both compounds were made. It was concluded that the diarsine existed in all three states only in the *trans*-conformation (C_{2h} symmetry) and it was suggested that the longer As-As bond distance (compared with the P-P bond distance) accounted for the existence of only the one isomer.

The photoelectron spectra of pyridine, phosphabenzene, arsabenzene, and stibabenzene have been reported [170]; the photoelectron spectrum of pyridine was known previously. The spectra of all four compounds were remarkably similar. Various spectral bands were assigned to molecular orbitals. *Ab initio* calculations were carried out for phosphabenzene, and it was concluded that for none of the occupied orbitals was there significant d orbital participation. Calculations for arsabenzene will appear in a later paper. There was a straight line relationship between the ionization potentials of the free atoms, N, P, As, and Sb, and the ionization potentials of the compounds.

Phospha- and arsagermacarbonanes, which contain three different hetero atoms in the cage, have been prepared by treating the sodium salts of the 7,8- and 7,9-$B_9H_9CHM^{2-}$ ions (where M = P or As) with germanium diiodide [171].

7. ARSONIC AND ARSINIC ACIDS

A series of compounds have been described by Trivedi and Mehta [172] formed by the condensation of sodium hydrogen *p*-aminobenzenearsonate (atoxyl) with a number of halogen compounds of the type XCH(CONHR)COMe and XCH(CONHR)CN, where X was Cl, Br or I and R was phenyl, a substituted phenyl group, or $PhCH_2$.

The Meyer reaction for the preparation of alkanearsonic acids is generally quite slow for longer chain alkyl groups. Luiggi and de Casal [173] have shown that *n*-butanearsonic acid can be prepared by heating As_2O_3 and *n*-BuBr in alkaline 10% aqueous glycerol solution for 30 hours.

A U.S. patent [174] for improving the preparation of arsanilic acid by the Béchamp reaction involved the reaction of aniline with arsenic acid under reduced pressure and by the hydrolysis of previously discarded by-products with strong acid.

Aliphatic arsonic amides or amido esters have been prepared by heating esters of aliphatic arsonic acids with an excess of a secondary amine in a nitrogen atmosphere [175]

The behavior of nine different methyl-, chloro-, or nitro-substituted arenearsonic acids (as well as benzenearsonic acid itself) on heating has been studied by means of differential thermal analysis [176]. These compounds lost any water of crystallization at temperatures of 140-250° and decomposed at 260-400°.

The pH and the Hammett acidity dependences of both the electronic absorption spectra and the fluoresence spectra of both $PhAsO_3H_2$ and $PhPO_3H_2$ were compared with those obtained from benzoic acid, phenol, toluene, and benzene [177]. The valence shell expansion behavior of both P(V) and As(V) in the two acids studied is quite similar to that of sulfur in naphthalenesulfonic acid and suggests that there is strong p_π-d_π interaction only in the excited state of the cationic species.

Tsentovskii and coworkers [178] have determined pKa values for a series of arenearsonic acids in dimethylformamide and dimethylsulfoxide and compared the resulting values with pKa values for these same acids in water. The influence of substituents in their effect on pKa values was in the same direction in the two organic solvents as in water, but a plot of pKa values in either solvent vs. pKa values in water gave a line whose slope was considerably greater than 45°, *i.e.* the organic solvents had a differentiating action on the ionization constants of these acids.

Thermodynamic ionization constants for a number of arenearsonic acids have been determined by Nualláin and Cinnéide [179]. Both potentiometric and spectrophotometric methods were used and the acids studied were benzenearsonic acid and the following substituted benzenearsonic acids: 2-OH, 2-OMe, 4-OMe, 2,4-$(OMe)_2$, 2-NH_2, 4-NH_2, 4-OH, and 2,4-$(OH)_2$. For the unsubstituted acid and the 4-OMe, 4-OH, and 4-NH_2 substituted acids a Hammett plot of ionization constant vs. σ values gave straight lines with a ρ value of 0.844 for the reaction $ArAsO_3H_2 \rightarrow ArAsO_3H^-$ and a ρ value of 0.840 for the reaction $ArAsO_3H^- \rightarrow ArAsO_3^=$. Sigma values of +0.972, +0.459, and -0.109 were calculated for the three substituents $-AsO_3H_2$, $-AsO_3H^-$, and $-AsO_3^=$, respectively. The pK_1 value for 2-$HOC_6H_4AsO_3H_2$ was 4.00 ± 0.02 compared with a value of 3.85 ± 0.02 for the 4-$OHC_6H_4AsO_3H_2$. This difference was attributed to intramolecular hydrogen bonding which increased the basicity of the AsO_3H_2 group. By contrast pK_1 for 2-$NH_2C_6H_4AsO_3H_2$ was 3.79 ± 0.02 compared with 4.13 ± 0.02 for pK_1 of the 4-substituted acid. This was attributed to hydrogen bonding between the NH and the As=O. In addition to pK_1 values pK_2 values were also obtained and it was concluded that in 2-$OHC_6H_4AsO_2H^-$ there was a hydrogen bond between the 2-OH group and

AsO_3H^-. In addition to the arsonic acid group pK values were also calculated for the OH groups and for NH_3^+ in the 2- and 4-substituted amino arsonic acids. It was concluded that the low basicity of the NH_2 group in $2\text{-}NH_2C_6H_4AsO_3H_2$ was the reason why this acid failed to form strong complexes with ferric or cupric ions.

It has been shown that the IR frequencies but not the band intensities of the AsO group for the compounds $p\text{-}RC_6H_4As(O)Et_2$ (where R = NO_2, Br, Cl, Me, H, OMe and NMe_2)correlated well with the Hammett σ-constants [180]. There was also correlation between UV wavelengths and the σ-constants. It was concluded that the As (as well as P) atom participated in conjugation with the phenyl ring.

Simon and Schumann [181] have reported on the Raman spectra from 200-3000 cm^{-1} and the IR spectra from 400-3800 cm^{-1} of $MeAsO_3H_2$, $EtAsO_3H_2$, $MeAsO_3HNa \cdot 1.5H_2O$, and $MeAsO_3D_2$ and assignments of the various bands have been made. It was concluded that the compounds probably possess C_s symmetry. It was also noted that the acids possessed strong hydrogen bonds.

In a second paper these same authors [182] report on the Raman and IR spectra of the Na and K salts of dimethylarsinic (cacodylic) and diethylarsinic acids. Several of these salts occurred in a hydrated form. It was concluded that the R_2AsO_2H skeleton probably possessed C_{2v} symmetry.

In a third paper the IR and Raman spectra of Me_2AsO_2H and of the same acid partially deuterated, and also of Et_2AsO_2H and of the reaction products of Me_2AsO_2H and Et_2AsO_2H with HCl were reported by Simon and Schumann [183]. It was concluded that both the free acids possessed C_s symmetry. The reaction of Me_2AsO_2H with HCl formed a hydrogen-bonded species $Me_2AsO_2H \cdots HCl$, whereas Et_2AsO_2H was protonated to form $[Et_2As(OH)_2]Cl$ which probably possessed C_{2v} symmetry. Assignments for the IR and Raman bands were made.

The absorption of several substituted arenearsonic acids, 10^{-4} M in concentration and in 0.01 and 2.0 M perchloric acid solution, were determined between 200 and 320 nm [184]. From these measurements wavelengths were chosen for the determination of the protonation constants for these acids. The existence of the protonated acids was demonstrated in $HClO_4$ solution between 0.01 to 3.00 M in concentration with a constant ionic strength of 2.99 M $NaClO_4$. The protonation constants for p-$HOC_6H_4AsO_3H_2$, o-$HOC_6H_4AsO_3H_2$, and 2,4-$(HO)_2C_6H_3AsO_3H_2$ were given. An accurate value for the protonation constant of $PhAsO_3H_2$ could not be determined.

A cobalt complex in which benzenearsonic acid was a ligand was prepared [185]. The complex had the structure $[Co(CS(NH_2)_2)_2(C_6H_5AsO_3H_2)Cl]$ and resulted from the interaction of the cobalt compound $COCl_2 \cdot (thiourea)_2$ and benzenearsonic acid.

A series of uranyl derivatives of benzenearsonic acid and substituted benzenearsonic acids has been described by Sandhu and Aulakh [186]. In these compounds the arsonic acid moiety appears to be acting as a tridentate ligand. Elemental analyses and IR spectral data were given. Sandhu and coworkers [187] have also described some copper(II) salts of o- and p-methoxy-, p-bromo-, and p-chlorobenzenearsonic acids and p-toluenearsonic acid and have listed IR spectral data and magnetic spectral data for these compounds. The ratio of Cu to arsonic acid is 1:1. On the basis of the IR data and the lack of solubility in non-coordinating organic solvents (solvents not given), the authors concluded that the compounds were probably polymeric with possibly octahedral geometry. In another paper from Sandhu's laboratory [130] ruthenium complexes in which benzenearsonic acid apparently served as either a monodentate or bidentate ligand have been described. The complexes were of the type $(PhAsO_2)Ru(CO)_2L_2$ and $(PhAsO_{2.5})_2Ru(CO)_2L'$, where $L = Ph_3P$, Ph_3As, $(p\text{-}MeC_6H_4)_3P$ or $(p\text{-}MeC_6H_4)_3As$ and $L' = Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, or $Ph_2As(CH_2)_4AsPh_2$. The C-O and As-O IR group frequencies were reported.

Braman and Foreback [188] have described a method for the determination of arsenite and arsenate ions and methanearsonic and dimethylarsinic acids in nanogram amounts. The method was then applied to various biological samples.

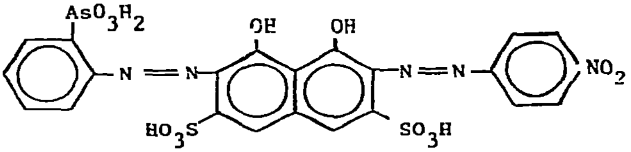
Dimethylarsinic and methylarsonic acids were found in natural waters, bird eggshells, seashells and in human urine. It was suggested that methylation was a method for the detoxification of inorganic arsenic in the animal body.

In an important paper Hassan and Elsayes [189] have shown that a variety of arenearsonic acids can be titrated in DMF solution with sodium methoxide in DMF and with brqmophenol red as the indication. Only one OH group of the arsonic acid was titrated and the error is quite small (from -0.4% to +0.1%). There was no interference from phenolic hydroxyl groups.

Nikuvashina and coworkers [190] have claimed that N-(*p*-arsonophenyl)-anthranilic acid is the indicator of choice for the titration of iron with potassium dichromate and that it can also be used for the titration of chromium with ferrous ammonium sulfate.

The synthesis of a new Arsenazo type reagent which differs in selectivity for rare earth elements has been described in the Russian chemical literature [191]. The new compound is 2-bis(carboxymethyl)aminomethyl-7-[(2-arsaphenyl)azo]naphtholamine-3,6-disulfonic acid and is termed arsenazokhimdu.

A new Arsenazo reagent named Arsenazo-*p*-NO_2(XXIII) has been synthesized and found to be a sensitive and selective reagent for the determination of lanthanum [192]. The UV spectrum of the new reagent was determined at several acidities.



XXIII

Talipov and coworkers [193] have obtained a new reagent for the determination of beryllium by coupling *o*-aminobenzenearsonic acid with salicylaldehyde. The compound was characterized by its IR spectrum and by elemental analyses but no results were given. It formed a 1:1 complex with beryllium sulfate which gave a brilliant green fluoresence. The fluoresence was at a maximum when the pH was adjusted to 5-6. The fluorescent spectrum of the complex was then used to determine the beryllium concentration with a high degree of sensitivity and accuracy.

Pietsch and Gilani [194] have shown that Zr and Ti can be extracted quantitatively from approximately 0.5 M HCl, H_2SO_4, or HNO_3 solutions by means of *n*-heptanearsonic acid in chloroform. The Zr or Ti can then be determined gravimetrically or, after some treatment, titrimetrically or photometrically.

The effect of an amine salt of diphenylarsinic acid on bean plants (decrease in plant growth and chlorophyl content) has been noted [195].

8. TERTIARY ARSINE OXIDES AND RELATED COMPOUNDS

Triaryl- or mixed arylalkylphosphine sulfides as well as triphenylarsine sulfide were converted to the corresponding phosphine or arsine oxides by refluxing with dimethyl sulfoxide in acid media (50% H_2SO_4) [196]. The yield of Ph_3AsO was 89%. The conversion of the phosphine sulfides to phosphine oxides occurred with inversion of configuration.

Gatilov and coworkers have also reported previously on the rearrangement of alkylarylarsine oxides when treated with alkyl halides. They now report [197] on the reaction of triethylarsine oxide with alkyl halides. A small amount of the alkyl arsinite is formed according to the equation:

$$Et_3AsO + RBr \rightarrow [Et_3AsOR]Br \rightarrow Et_2AsOR + EtBr$$

(where R = Et, *n*-Pr, or *n*-Bu)

The principal product of the reaction was a hydroxyarsonium tribromide which the authors suggest was formed as follows:

$$[Et_3AsOCH_2CH_2R]Br \rightarrow Et_3AsO + \overset{+}{C}H_2CH_2R \rightarrow [Et_3AsOH]Br_3 + CH_2{=}CHR$$

The structure of this hydroxyarsonium salt was confirmed by NMR spectra. Gatilov and Perov [198] have also studied the reaction of tri-*n*-propylarsine oxide with acetyl chloride. The reaction presumably proceeded through an intermediate arsonium compound which was not isolated:

$$n\text{-Pr}_3\text{AsO} + \text{MeCOCl} \rightarrow [\text{Pr}_3\text{AsOCOMe}]\text{Cl} \rightarrow n\text{-Pr}_2\text{AsOCOMe} + n\text{-PrCl}$$

The mixed anhydride was characterized by elemental analyses and IR spectra. The reaction of tri-*n*-propylarsine oxide with various alkylbromides led to the formation of an alkyl arsinite, Pr_2AsOR, and a hydroxyarsonium salt, $[Pr_3AsOH]Br$.

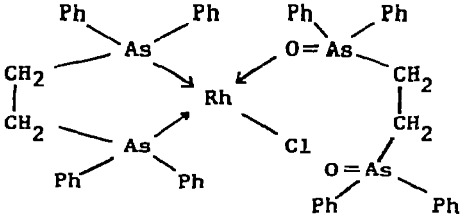
In order to further elucidate the mechanism of the reaction of tertiary arsine oxides with alkyl iodides Chernokal'skii and Vorob'eva [199] have studied the kinetics of the reaction. The pKa values for the conjugate acids of a number of the arsine oxides were determined. There was a linear relationship between the second order rate constants and the pKa values obtained. It was concluded that the reaction was an S_N2 reaction.

On the basis of earlier empirical assignments of IR and Raman spectra of many organoarsenic compounds, Lamanova and Shagidullin [200] calculated a set of force constants for the compounds Me_3AsO and $(MeO)_3AsO$ which enabled them to predict values for the As=O, As-O and As-C absorptions in the IR and Raman spectra. There was fairly good agreement between these calculated values and the found values for the absorption frequencies. For example, the calculated values for the As=O bond in Me_3AsO and $(MeO)_3AsO$ were 903 and 976 cm^{-1}, respectively, whereas the found values were 929 and 933 cm^{-1}. The absorption found at 580 cm^{-1} was assigned to the As-C bond.

In a paper described in detail under Antimony, the two arsenic-containing compounds $[Ph_3Sb(Ph_3AsO)_2](ClO_4)_2$ and $[Me_3Sb(Ph_3AsO)_2](ClO_4)_2$ were described [201].

Complexes of the type $R_nO \cdot BF_3$, where R_nMO represented molecules such as R_2SO, R_3NO, R_3PO, and R_3AsO (R = an alkyl group), were prepared by Bravo and coworkers [202] and their ^{11}B, ^{19}F, and ^{31}P NMR spectra were reported. The arsenic compounds were $R_3AsO \cdot BF_3$ where R = Me, Et, *n*-Pr and *n*-Bu. The coupling constants J_{B-F} were found to decrease in the order $R_2SO \cdot BF_3$ > $R_3NO \cdot BF_3 \simeq R_3PO \cdot BF_3 > R_3AsO \cdot BF_3$. These results suggested that R_3NO was a better donor than R_3AsO.

It has been shown by Poddar and Agarwala [203] that the rhodium complex $Rh(Ph_3P)_3Cl$ acts as a catalyst for the oxidation of tertiary arsines and phosphines by molecular oxygen. Thus both Ph_3As and $Ph_2AsCH_2CH_2AsPh_2$ are oxidized by molecular oxygen in the presence of the rhodium compound but not in its absence. The diarsine is oxidized to $Ph_2AsCH_2CH_2As(O)Ph_2$. In addition the rhodium complex XXIV was isolated.



XXIV

Several papers have appeared in which trialkyl- or triarylarsine oxides have served as ligands to gold [204] or uranium [205-207].

9. ARSONIUM COMPOUNDS AND ARSENIC YLIDS

A number of triphenylalkylarsonium, stibonium, and phosphonium salts of the type $[Ph_3MCH_2R]X$, where M = As, Sb, or P, R = H, Ph, COMe, CO_2Me, CO_2Et, and COPh, and X = NO_3^-, BF_4^-, PF_6^-, BPh_4^-, I^-, I_3^-, and Br^-, were prepared [208]. The arsonium and stibonium salts formed contact ion pairs even with very large anions in acetone and in chloroform as determined by molecular weight data. The ^1H NMR spectra of the compounds were determined in methylene chloride. In the case of the tetraphenylborates the aromatic ring current of the phenyl rings in the tetraphenylborate anion causes the protons in the methylene groups attached to As or Sb to shift upfield by 1 to 3 ppm.

The synthesis of long chain quaternary ammonium, phosphonium, and arsonium hydroxides from the corresponding halides by treatment with sodium hydroxide at the interface between water and an immiscible solvent such as kerosene and isooctyl alcohol has been described [209]. The two arsonium hydroxides prepared were $(n\text{-}C_8H_{17})_4AsOH$ and $CH_3(n\text{-}C_8H_{17})_3AsOH$. The starting tetraalkylarsonium halides were also new compounds but were prepared by known methods.

The reaction of Ph_4AsCl with lithium dialkylamides of the type R_2NLi (where R_2N = Et_2N, piperidino, morpholino, or Ph_2N) in the presence of $(Me_2N)_3PO$ gave Ph_3As and $PhNR_2$ [210]. The results varied somewhat with the solvent used and a free radical mechanism was suggested.

The reaction of $[Ph_4As][TeCN]$ with Ph_3P to form $Ph_3PTePPh_3$ has been described by Austad and coworkers [211].

A number of alkylmethyldiphenyl- and alkylallyldiphenylarsonium iodides have been synthesized by Tsentovskii and coworkers [212] from methyldiphenyl- or allyldiphenylarsines and the appropriate alkyl iodides. The equivalent conductances of these salts in acetone solution were determined. There was considerable deviation between observed and calculated values for the Onsager slope of conductance/concentration which indicated the association of these ions in solution. In general there was less association with those salts that had branched chains at the arsenic atom. A number of the alkylmethyldiphenylarsonium iodides were converted to the corresponding arsonium perchlorates by reaction of the iodides with magnesium perchlorate in aqueous acetone [213]. The IR spectra were identical with those of the corresponding iodides except for the spectrum of the perchlorate ion.

Because cryoscopic molecular weight determinations of $TeCl_4$ in benzene solution have indicated the presence of an equilibrium between $(TeCl_4)_4$ and lower molecular weight species, Krebs and Paulat [214] report on their attempts to isolate derivatives of these lower molecular weight compounds. Among the compounds reported was $[Ph_4As]_2[Te_2Cl_{10}]$ as a yellow crystalline compound which was analytically pure.

Vetter and Klar [215] have described the preparation and properties of the nitrosolate ions $RC(N=O)=NO^-$, where R = Me or Ph. Among the cations used was the tetraphenylarsonium ion.

The preparation of three isomeric tetraphenylarsonium *trans*-(dithiocyanato)bis(dimethylglyoximato)cobaltate(III) has been described by Epps and Marzilli [216]. The compounds differed only in the mode of attachment of the SCN groups and IR and ^1H NMR spectra were used in assigning the structures.

The tetraphenylarsonium salts $[Ph_4As][Ir(CO)_2X_2]$, where X = Cl, Br, or I, were prepared by Piraino and coworkers [217], and their reactions with mono- and bidentate ligands including $Ph_2AsCH_2CH_2AsPh_2$ were studied.

Two interesting compounds of niobium and tantalum, $[(Nb_6Cl_{12})Cl_6][Ph_3AsOH]_2$ and $[(Ta_6Cl_{12})Cl_6][Ph_3AsOH]_2$, containing the protonated triphenylarsine oxide cation were prepared by Field and coworkers [218]. The crystal structure of the niobium compound was determined. Interatomic distances and angles for the arsonium cation were given.

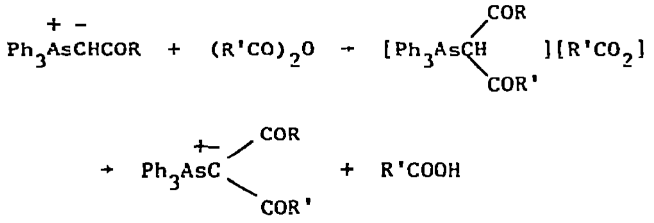
The crystal structure of bis(tetraphenylarsonium) tris-(*cis*-1,2-dicyano-1,2-ethylenedithiolato)iron(IV) has been determined by Sequeira and Bernal [219]. Although the arsonium cations are tetrahedral, the overall symmetry is C_1, probably because the phenyl rings are rotated to accomodate the packing in the crystal lattice. The average As-C bond length is 1.901Å in agreement with previous determinations.

In another determination of the crystal structure of the tetraphenylarsonium cation, Brown and Stiefel [220] have examined the crystal structure of bis(tetraphenylarsonium) tris(1,2-dicyanoethylenedithiolato)molybdenate(IV) $[Ph_4As]_2\ [Mo(S_2C_2(CN)_2)_3]$ and its tungsten analog. Bond distances and angles for the tetraphenylarsonium ion were given which are in agreement with other recent determinations.

The X-ray crystal structure of the compound $(Ph_4As)_2Cu_2Cl_6$ established the presence of $Cu_2Cl_6^{2-}$ units ionically bound to tetraphenylarsonium ions [221].

The complex *cis*-$(Ph_4As)_2[RuCl_4(CO)_2]$ was prepared from $[RuCl_2CO(C_7H_8)]_n$ and $Ph_4AsCl{\cdot}HCl$, where C_7H_8 was norbornadiene [222].

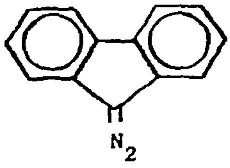
In a long and detailed paper Gosney and Lloyd [223] have described the preparation of a large series of arsonium ylids and have studied their IR, UV, ^1H NMR and mass spectra. Several methods were used for preparing these ylids. In one method triphenylarsine oxide was condensed with compounds containing an active methylene group either in refluxing acetic anhydride or by refluxing in triethylamine in the presence of P_4O_{10}. Yields by both methods were usually excellent and the reaction failed only where the reactive methylene compound was $(EtO_2C)_2CH_2$. A total of 16 ylids were obtained by this method. The structure of these ylids was confirmed in a number of cases by an alternative synthesis involving acylation of a mono-β-ketoylid:



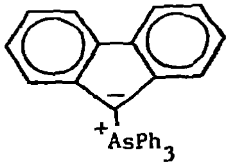
$$Ph_3\overset{+}{As}\overset{-}{C}HCOR + (R'CO)_2O \rightarrow [Ph_3AsCH\begin{smallmatrix}COR\\COR'\end{smallmatrix}][R'CO_2]$$
$$\rightarrow Ph_3\overset{+}{As}\overset{-}{C}\begin{smallmatrix}COR\\COR'\end{smallmatrix} + R'COOH$$

Several instances are mentioned where anomalous results were obtained by any one of the above three methods.

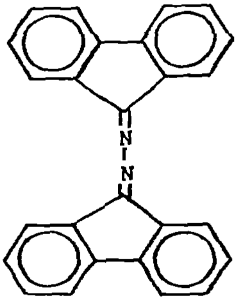
Yet another method for preparing the arsonium ylids involved the thermal decomposition of the appropriate diazocyclopentadiene in the presence of triphenylarsine in a nitrogen atmosphere. The reaction was catalysed by copper or a copper(I) salt. The reaction was believed to involve formation of a carbene which reacted with the arsenic lone pair. The ylid $Ph_3\overset{+}{As}C^{-}(CO_2Et)_2$, which could not be prepared from the arsine oxide, was obtained in 61% yield by this method. The reaction was unsuccessful with the diazo compound XXV where XXVI was obtained rather than the expected ylid XXVII.



XXV



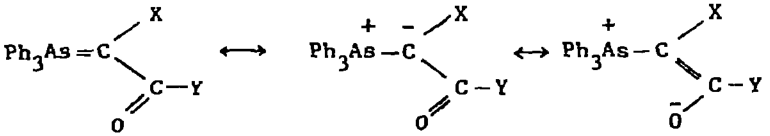
XXVII



XXVI

It was suggested that XXVII was formed but then reacted further with XXV with elimination of Ph_3As and formation of XXVI. The ylids were found to be non-hygroscopic crystalline solids and with a few exceptions were stable indefinitely in air and in solution. They were recovered unchanged after heating in ethanolic sodium hydroxide.

The IR, UV, and ^1H NMR spectra were obtained and were discussed in considerable detail. From the NMR data it was concluded that the main contributing conformations were the *cisoid* (Z) forms as follows:



The mass spectra were determined and detailed fragmentation pathways were given.

Only one of the ylids $Ph_3\overset{+}{A}s-\overset{-}{C}(CO_2Et)_2$ reacted with benzaldehyde by the Wittig reaction to form $PhCH=C(CO_2Et)_2$ and Ph_3AsO. Many of the ylids, however, reacted with *p*-nitrobenzaldehyde to give the alkene and Ph_3AsO. There was no evidence for the formation of epoxides with any of the ylids in their reaction with aldehydes. It was also concluded that the arsonium ylids were more reactive than their phosphonium or sulfonium analogs. This was explained as due to the greater contribution of the dipolar canonical form to the structure of the arsonium ylids.

It is known that non-stablized arsenic ylids of the type $Ph_3As{=}CHR$ (R=H or Me) react with carbonyl compounds to give epoxides, whereas stabilized ylids of the type $Ph_3As{=}CHCOR$ give olefins with carbonyl compounds. Ylids of the type $Ph_3AsCHC_6H_4X$-*p* are termed semi-stabilized ylids and can give either epoxides or olefins with carbonyl compounds. Kendurkar and Tewari [224] have investigated the reaction of the ylid $Ph_3As{=}CHC_6H_4NO_2$-*p* with a large variety of aldehydes and ketones. With the exception of acetophenone,which failed to react with the ylid, the sole reaction product in each case was the olefin. The yields varied between 65 and 94%. No epoxides were obtained. The exclusive formation of olefins was attributed to the stabilizing effect of the electron-withdrawing *p*-nitro group. The ylid was also treated with several acyl halides to form new stabilized ylids of the type $Ph_3As{=}C(COR)C_6H_4NO_2$-*p*, where R=Me, Ph, $4\text{-}NO_2C_6H_4$, and $2,5(NO_2)_2C_6H_3$.

In a paper devoted to the mechanism of the Wittig reaction, N.A. Nesmeyanov and coworkers [225] have compared the rate constants and activation parameters for a series of stable ylids of both phosphorus and arsenic in their reaction with two different aldehydes in xylene solution. They concluded that the mechanism of the reaction of P and As ylids with aldehydes is the same and that it is essentially a one-step reaction.

Several methods for preparing the little-known triphenylarsinimines $Ph_3As{=}NR$, where $R{=}C_6F_5$, 4,6-dimethylpyrimidyl, $-CO_2Et$, *p*-$MeC_6H_4SO_2$, $MeSO_2$, CN, PhCO, and *p*-$NO_2C_6H_4CO$, have been successfully tried [226]. One method involves reaction of an azide at its decomposition point with a melt or with a solution of triphenylarsine:

$$XN_3 \xrightarrow{\Delta} XN \xrightarrow{Ph_3As} Ph_3As{=}NX$$

The formation of an intermediate nitrene was suggested and the reaction was catalysed by small amounts of copper. Thermolysis of 3-phenyl-1,4,2-dioxolidin-5-one, known to give benzoyl nitrene on heating, gave with Ph_3As, Ph_3AsO and Ph_3CN. It was suggested that these products arose by decomposition of $Ph_3As{=}NCOPh$. In another reaction $Ph_3As{=}NCO_2Et$ and $Ph_3As{=}NSO_2C_6H_4Me$-*p* were obtained by base induced α-elimination from *p*-nitrobenzenesulfonoxyurethane and N-*p*-nitrobenzenesulfonoxytoluene-*p*-sulfonamide, respectively, in the presence of triphenylarsine. Again it was suggested that a nitrene was formed.

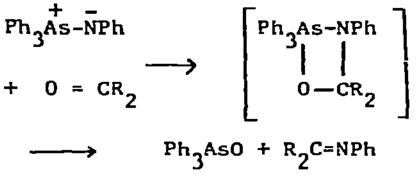
In yet another reaction methane- and *p*-toluenesulfonamides and benzamide were allowed to react with Ph_3As in the presence of $Pb(OAc)_4$ in methylene chloride. The arsinimines were obtained in satisfactory yields in all cases. In these reactions it was shown that nitrenes were not involved but rather that $Ph_3As(OAc)_2$ was formed which reacted with the amide:

$$Ph_3As(OAc)_2 + XNH_2 \rightarrow Ph_3As{=}NX + 2HOAc$$

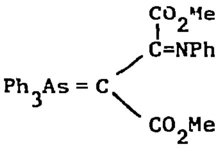
Subsequently the diacetate $Ph_3As(OAc)_2$ was isolated and characterized and found to react with amides in the manner indicated.

Dale and Frøyen [227] have reported on the electron impact-induced fragmentation of four stable arsonium ylids of the type $Ph_3As{=}CRCOX$, where (R,X) = (H,Me), (H,Ph), (H,OMe), and (CN,OMe), and compared their results with the corresponding phosphonium ylids. All of the arsenic ylids showed peaks characteristic of the fragmentation of Ph_3As, and all four ylids showed the presence of the ions M^{+}, $(M-1)^{+}$ and $(M-X)^{+}$ in the spectra. These latter results were generally quite similar to the corresponding phosphorus ylids. However, in the case of $Ph_3As{=}CHCO(OMe)$ and its phosphorus analog, there was considerable difference between their fragmentation patterns.

Triphenylarsine phenylimine $Ph_3As{=}NPh$ reacts with a variety of compounds such as carbonyl compounds, isocyanates, isothiocyanates, nitroso compounds, carbon disulfide, sulfur dioxide, dimethyl acetylenedicarboxylates and nitrile oxides [228]. In the case of carbonyl compounds the reaction was believed to be similar to a Wittig reaction:

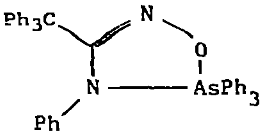


With dimethyl acetylenedicarboxylate the product is XXVIII.



XXVIII

With triphenylacetonitrile N-oxide $Ph_3C-C\equiv N-O$, the product is XXIX.



XXIX

The anion radical salt tetraphenylarsonium 7,7,8,8-tetracyanoquinodimethane (As-TCNQ) has been the subject of numerous ESR investigations. In a paper by Deutschbein and coworkers [229] measurements of dynamic proton polarization were used to characterize the paramagnetic states of the anion radical. It was concluded that the different paramagnetic states were characterized not only by their spin quantum numbers, but also signifigantly by other properties. Another paper from this same laboratory deals with the ESR spectrum of this same compound at 77 and at 373°K [230].

An electron microscope study of the most important crystal faces of the TCNQ (tetracyanoquinodimethane) complex salts of the triphenylmethylphosphonium and triphenylmethylarsonium cations has been reported [231].

In a continuation of studies of the anion radical salts $[Ph_3PMe]^+_{1-X}[Ph_3AsMe]^+_X[TCNQ]^{\overline{\cdot}}$ where ($0 \leq X \leq 1$) and TCNQ = 7,7,8,8-tetracyanoquinodimethane, Suzuki and Iida[232,233] have reported on the temperature dependence of the ESR zero-field splitting parameters which are associated with the transition between the ground and a low-lying triplet excited state. The authors concluded that the application of ESR and its variation with temperature brings valuable knowledge concerning the phase transitions of the TCNQ anion radical salts.

In addition to the ESR studies of Suzuki and Iida, Iida [234] has reported on the electrical conductivity of these radical anion salts as a function of temperature. With the exception of the salt where X = 1.00, all of these salts were found to show a sharp discontinuity in the temperature dependence of the electrical conductivity. Both the transition temperature and the magnitude of the discontinuity were determined as a function of the composition parameter, X.

10. COMPOUNDS WITH As-S BONDS

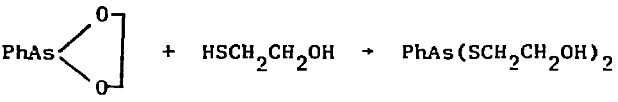
Müller and coworkers [235] have prepared the three thioarsinic acids $Ph_2As(O)SH$, $(PhCH_2)_2As(O)SH$, and $(PhCH_2)_2As(S)SH$ from diphenylarsinic and dibenzylarsinic acids, respectively. The last compound was obtained by the action of H_2S on potassium dibenzylarsinate in ethanol solution, whereas the other compounds were obtained from the potassium arsinates by the action of H_2S in aqueous solution. These acids gave tetrahedrally coordinated complexes of the type ML_2 where M = Co, Zn, or Cd, and L was the thioarsinic acid. The compounds were characterized by elemental analyses, electronic spectra, and magnetic measurements.

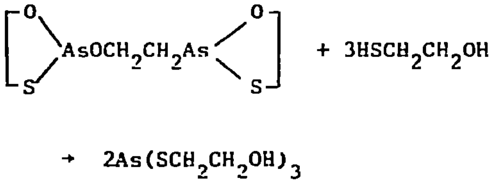
A long synthetic paper on the preparation and properties of esters of trivalent arsenic thioesters has been published by Chadaeva and coworkers [236]. The esters had the general formula $R_nAs(SCH_2CH_2OH)_{3-n}$ and were obtained by the following general reaction:

$$R_nAs(XR')_{3-n} + 3\text{-}n(HSCH_2CH_2OH) \rightarrow R_nAs(SCH_2CH_2OH)_{3-n} + 3\text{-}nR'XH$$

where X = O or S, R = an alkyl or aryl group, and R' = Me or Et. The esters were all obtained as viscous liquids which with the exception of $As(SCH_2CH_2OH)_3$ could all be distilled *in vacuo*. Their IR spectra and elemental analyses were reported. Their reaction with oxidizing agents, acyl halides, alkyl halides, and several phosphorus and arsenic compounds (arsines, alkyl alkylarylarsinites, phenyldichloroarsine, dialkyl arylarsonites, and dialkyl arylphosphonites) as well as their behavior on pyrolysis to yield 1,3,2-oxathiarsolanes has been given in considerable detail.

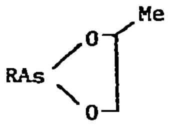
Chadaeva and coworkers [237] have reported that the 1,3,2-oxathiarsolane ring is readily opened by reaction with mercaptans:





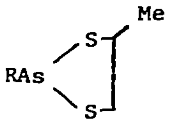
Mercaptans other than 2-mercaptoethanol also opened the ring, but the products could not always be isolated in a pure state.

An NMR study of the four 1,3,2-dioxarsolanes (XXX) and 1,3,2-dithiarsolanes (XXXI) has been made by Aksnes and Vikane [238].
The ^1H NMR spectra were analyzed on the basis of an $ABCD_3$ spin system and it was shown that the compounds existed as a mixture of *cis*- and *trans*-isomers due to configurational stability about the arsenic atom. The *trans*-form predominated. The five-membered rings were adequately described in



XXX

(R = Cl or Ph)



XXXI

terms of twist-envelope conformations which are in equilibrium, although the *cis*-form apparently preferred one conformation.

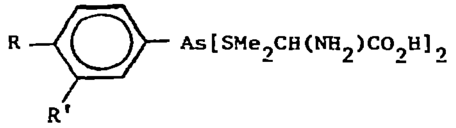
Because of contradictory results obtained by different investigators for the reaction of alkyldiaryl-, dialkylaryl- or trialkylarsine sulfides with acyl halides, Gatilov and coworkers [239] have made a careful study of the reaction between diethylphenyl-, triethyl-, and tri-*n*-propylarsine sulfides with acetyl choride. At 80° in benzene only (acetylthio)ethylphenylarsine was formed but in acetone the intermediate quasi-arsonium salt could be isolated:

$$\begin{aligned} Et_2PhAsS + MeCOCl &\rightarrow [Et_2PhAsSCOMe]Cl \\ &\rightarrow EtPhAsSCOMe + EtCl \end{aligned}$$

When the intermediate arsonium compound was heated in benzene the (acetylthio) ethylphenylarsine was formed. With triethyl- and tri-*n*-propylarsine sulfides the intermediate arsonium salts were also isolated, and these also gave the $R_2AsSCOMe$ compounds on heating in benzene.

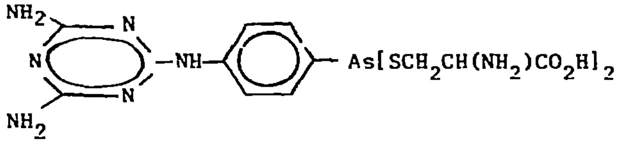
Two new ligands, $Ph_2As(O)CH_2CH_2As(O)Ph_2$ and $Ph_2As(S)CH_2CH_2As(S)Ph_2$, were synthesized by Mani and Scozzafava [240]. The oxide was obtained by oxidation of the corresponding arsine with hydrogen peroxide, whereas the sulfide by reaction of the arsine with excess sulfur. A number of complexes obtained by reaction of these two ligands with various Co(II) and Ni(II) compounds were described. Reflectance spectra as well as UV and IR spectra for the complexes were given.

A German patent claims the preparation of organic arsenicals of the type XXXII which were useful in the treatment of filariasis and trypanosomiasis [241].



XXXII

In one compound R = 4,6-diamino-2-triazinylamino and R' = H, in another compound R = OH, R' = NH_2. Another German patent [242] describes the use of the arsenical XXXIII as a filaricidal agent.



XXXIII

The CO stretching bands and the ^1H NMR data for methyl protons for complexes of the type $M(CO)_5 \cdot Me_3AsS$, where M = Cr or W, have been reported by Ainscough and coworkers [243]. Spectra of the complex $W(CO)_5 \cdot Ph_3AsO$ and of a number of complexes containing various phosphine sulfide ligands were also reported.

Both the IR and Raman spectra of Me_3AsS and Me_3AsSe and their perdeuterated analogs have been reported by Kolar and coworkers [244]. Assignments of 22 of 24 fundamental vibrational frequencies were made and a normal coordinate analysis was carried out. By calculating the potential energy distribution for each molecule, it was shown that there was very little coupling between the different modes. From the found values of the force constants the bond orders of 1.43 and 1.40 were calculated for the AsS and AsSe bonds, respectively. This compares with the known value of 1.60 for the AsO bond.

The palladium and platinum complexes $Pd(NCS)_2 \cdot 2Ph_3AsS$ and $Pt(NCS)_2 \cdot Ph_3AsS$

have been prepared by extraction of an aqueous solution of $K_2Pd(SCN)_4$ or $K_2Pt(SCN)_4$ with a chloroform solution of Ph_3AsS [245]. The compounds were characterized by elemental analyses and IR spectra.

The ESR spectrum of the oxovanadium(IV) complex $VO(S_2AsMe_2)_2$ formed by the reaction of sodium dimethyldithioarsinate with $VOCl_2$, has been determined by McCormich and coworkers [246]. There is superhyperfine splitting in the spectrum of the complex which was attributed either to direct vanadium 3d-arsenic 4s, 4p interaction or to delocalization of the unpaired electron onto the arsenic atom *via* metal-sulfur interaction. The authors were unable to assess the relative importance of these two mechanisms

In a paper dealing largely with Me_3PS, Me_2PhPS, and similar compounds as ligands to rhodium and iridium, the compound $[(cod)IrCl(Me_3AsS)]$, where cod = cycloocta-1,5-diene, was described and its IR and ^1H NMR spectra were given [247].

11. MISCELLANEOUS

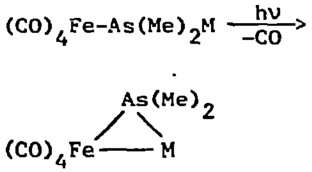
Ehrl and Vahrenkamp [248] have previously described the preparation of the complex $(CO)_5CrAs(Me)_2Cl$. These same authors now have described [249] the reaction of this complex with the sodium derivatives NaM where M = $Mo(CO)_3C_5H_5$, $W(CO)_3C_5H_5$, $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2C_5H_5$, and $Co(CO)_4$. The reaction was carried out in THF solution at room temperature to give the arsenic-bridged complexes $(CO)_5CrAs(Me)_2M$. These complexes were stable towards air and moisture and possessed fairly low m.p.'s. Thermally or photochemically the arsenic-chromium bond was split with the formation of chromium hexacarbonyl:

$$(CO)_5CrAs(Me)_2M(CO)_n \xrightarrow{h\nu} Cr(CO)_6 + 1/2\ [Me_2AsM(CO)_{n-1}]_2$$

The ^1H NMR and IR spectra of the new complexes were given.

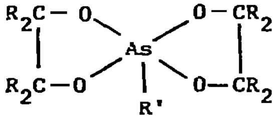
In a later paper Ehrl and Vahrenkamp [250] reported a group of interesting arsenic-bridged dinuclear complexes containing arsenic-iron bonds. The initial reaction involved the formation of a distillable iron-arsenic complex, $(CO)_4FeAs(Me)_2NMe_2$, by the interaction of $Fe_2(CO)_9$ and Me_2AsNMe_2 in benzene solution at room temperature. Reaction of this compound with HCl gave the crystalline (m.p. 33-34°) compound $(CO)_4FeAs(Me)_2Cl$. The reaction of this complex with sodium derivatives of Mo, W, Mn, and Co gave the arsenic-bridged complexes $(CO)_4FeAs(Me)_2Mo(CO)_3C_5H_5$, $(CO)_4FeAs(Me)_2W(CO)_3C_5H_5$, $(CO)_4FeAs(Me)_2Mn(CO)_5$, $(CO)_4FeAs(Me)_2Fe(CO)_2C_5H_5$, and $(CO)_4FeAs(Me)_2Co(CO)_4$. The ^1H NMR and the IR spectra of these arsenic-bridged complexes as well as the spectra of the two complexes $(CO)_4FeAs(Me)_2NMe_2$ and $(CO)_4FeAs(Me)_2Cl$ were given. The mass spectrum of the complex $(CO)_4FeAs(Me)_2Co(CO)_5$ was also given. It was also found that the chloro compound $(CO)_4FeAs(Me)_2Cl$ underwent hydrolysis to form the complex $(CO)_4FeAs(Me)_2OAs(Me)_2Fe(CO)_4$.

Ehrl and Vahrenramp [251] also found that the complexes of the type $(CO)_4FeAs(Me)_2M$ (where M = $Mo(CO)_3C_5H_5$, $W(CO)_3C_5H_5$, $Mn(CO)_5$ and $Co(CO)_4$) described in the previous paper underwent photolysis to form new arsenic-bridged heteronuclear complexes with metal-metal bonds. The reaction involved was:

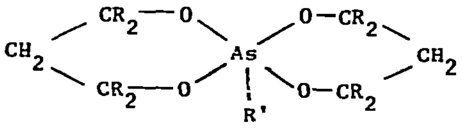


The resulting heteronuclear complexes were red to orange in color, stable in the air and were quite volatile. Their m.p.'s varied between 115° and 145°. The ^1H NMR, IR, and mass spectra of the complexes were given.

Several spirocyclic esters of the type XXXIV and XXXV have been prepared by Gamayurova and coworkers [252] from arsonic acids and glycols.



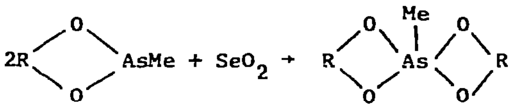
XXXIV



XXXV

The yields of esters with the 5-membered rings were considerably larger than yields of esters with 6-membered rings. The presence of the 1,3,2-dioxarsolane ring was confirmed by IR spectrocopy.

Although the oxidation of esters of arsonous acids $RAs(OR)_2$ with selenium dioxide gives esters of the corresponding arsonic acids, Wieber and coworkers [253] have shown that oxidation of the cyclic esters XXXVI with SeO_2 gave spirocyclic compounds:



XXXVI XXXVII

$+ 1/n[MeAs(O)-O]_n + Se$

(R = $-CMe_2CMe_2-$, $-CHMeCHMe-$, $-CH_2CH_2-$, o-C_6H_4-)

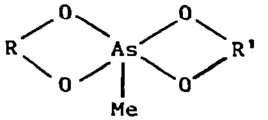
In order to avoid formation of the polymeric methanearsonic acid anhydride the reaction was run in the presence of a diol:

$$\text{XXXVI} + R(OH)_2 + 1/2SeO_2$$

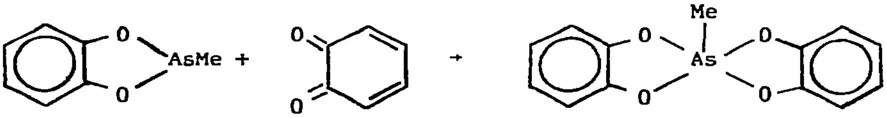
$$\rightarrow \text{XXXVII} + 1/2\ Se$$

It was also possible to prepare unsymmetrical spirocyclic compounds by this reaction:

$$\text{XXXVI} + R'(OH)_2 + 1/2SeO_2 \rightarrow$$



In yet another reaction it was found possible to react the cyclic arsonous acid esters with quinones to give either symmetrical or unsymmetrical spirocyclic compounds. For example a symmetrical spirocyclic compound was prepared as follows:



The reaction of bis(trifluoromethyl)nitroxyl with $(CF_3)_2AsMe$ proceeded according to the following two equations [254]:

$$(CF_3)_2AsMe + 2(CF_3)_2NO \rightarrow [(CF_3)_2NO]_2As(CF_3)_2Me$$

$$(CF_3)_2AsMe + 2(CF_3)_2NO \rightarrow (CF_3)_2NOAsCF_3Me + (CF_3)_2NOCF_3$$

The product in the first reaction exists in two isomeric forms with m.p.'s of 22° and 33° *in vacuo*. With Me_2AsCF_3 and $(CF_3)_2NO$ only one product $[(CF_3)_2NO]_2AsMe_2CF_3$ was obtained. All such As(V) compounds were cleaved by HCl:

$$[(CF_3)_2NO]_2AsMe_3 + 2HCl \rightarrow (CF_3)_3AsCl_2 + 2(CF_3)_2NOH$$

Manganese and rhenium pentacarbonyls with 2,3,4,5-tetraphenylarsole form the compounds $Ph_4C_4AsM(CO)_5$ [255]. These compounds (M = Mn or Re) lose carbon monoxide on heating or irradiation to form the dimeric compounds $[Ph_4C_4AsM(CO)_4]_2$ which on further heating or irradiation give $Ph_4C_4AsM(CO)_3$. The structure of the manganese compound $Ph_4C_4AsMn(CO)_3$

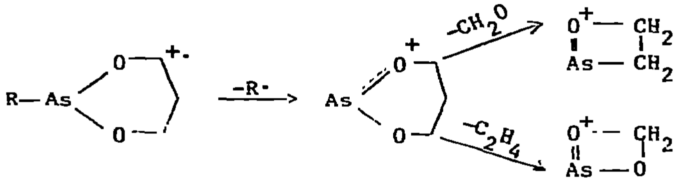
was determined by means of an X-ray diffraction study. The arsole ring system is π-bonded to the manganese tricarbonyl grouping with the plane containing the carbonyl groups essentially parallel to the arsole ring. The Mn-As distance, however, is shorter by 0.1A than the sum of the covalent radii. The As-C (ring) distances were also shorter than expected. The authors therefore concluded that there was extensive delocalization throughout the arsole ring. This resulted in considerable angular distortion within the planar ring.

In a paper [256] devoted to the preparation of organometallic derivatives of 1,6- and 1,10-dicarba-*closo*-decacarboranes by means of the corresponding lithio derivatives, one arsenic compound tris(1-phenyl-1,10-dicarba-*closo*-decaboran-10-yl)arsine was reported. The compound was characterized by elemental analyses but no spectral data were given.

An investigation of the IR and Raman spectra of the *o*-, *m*-, and *p*-carbaphosphaboranes and carbaarsaboranes has been carried out by Vinogradova and coworkers [257]. In addition, the IR spectra of the two C-deuterated *m*-isomers were obtained. The C-H bond in both the phospha- and arsaboranes is capable of H-bonding; the enthalpy of this bond in Me_2SO solution was 2-3 kcal/mole.

The interesting compound $NaAs(Me_2)(BH_3)_2$ has been obtained by Schwartz and Keller [258] by the interaction of Me_2AsNa and B_2H_6 in ether solution. It was obtained as colorless hygroscopic crystals containing 0.5 mole dioxane With B_2D_6 in ether solution the compound underwent proton-deuterium interchange. It reacted with $[Me_3NH]Cl$ in monoglyme to form $Me_2NBH_2As(Me_2)BH_3$. This latter compound on pyrolysis yielded Me_3NBH_3 and Me_2AsBH_2.

The mass spectra of a series of 2-alkyl-1,3,2-dioxarsenanes, as well as 2-phenyl-1,3,2-dioxarsenane and several 1,3,2-dioxarsenanes substituted in the ring, have been investigated by Frøyen and Møller [259]. With the alkyl-substituted compounds the main fragmentation mode involves loss of an R· group from the molecular ion followed by loss of CH_2O or C_2H_4:



Where R = Ph the above process is in competition with a direct loss of $C_6H_5As^{+\cdot}$. The presence of substituents in the 1,3,2-dioxarsenane ring markedly alters the fragmentaion pathway. In the case of 2-phenyl-5,5-dimethyl-1,3,2-dioxarsenane there is a marked decrease in the abundance of the molecular ion. The chemical syntheses of the compounds were not described and will be published in a separate paper.

Anderson and Drake [260] have reported the synthesis of secondary arsines containing the Ge-As bond. They were prepared by several different methods:

$$(Me_3Ge)_2AsR + MeLi \rightarrow Me_4Ge + LiAsRGeMe_3$$

$$LiAsRGeMe_3 + MeSH \rightarrow LiSMe + Me_3GeAsHR$$

$$Me_3GeBr + LiAsHR \rightarrow LiBr + Me_3GeAsHR$$

$$4Me_3GeBr + LiAlH(AsHMe)_3 \rightarrow LiBr + Me_3GeH + 3Me_3GeAsHR$$

(where R = Me or Ph).

By reaction of these secondary arsines with trimethylstannyldimethylamine mixed germanium-tin arsines were obtained:

$$Me_3GeAsHR + Me_3SnNMe_2 \rightarrow Me_3Ge(Me_3Sn)AsR + Me_2NH$$

$$(R = Me_3Ge,\ Me\ or\ Ph)$$

These products underwent redistribution to the symmetrical arsines:

$$2Me_3Ge(Me_3Sn)AsR \rightarrow (Me_3Ge)_2AsR + (Me_3Sn)_2AsR$$

In yet another reaction mixed germanium-tin arsines were prepared:

$$Me_2M(NMe_2)_2 + 2(Me_3Ge)_2AsH \rightarrow [(Me_3Ge)_2As]_2MMe_2 + 2Me_2NH$$

$$(M = Ge \text{ or } Sn)$$

The authors were unable to prepare mixed silicon-germanium arsines. Both NMR and IR spectra for the new compounds were reported.

ESR data for radicals of the type $R_2\dot{C}CH_2PR_3^+$ and $R_2\dot{C}CH_2AsR_3^+$ have nearly isotropic hyperfine coupling to ^{31}P and ^{75}As that corresponds to approximately 3.7% s-character [261]. By contrast the phosphine and arsine radicals $R_2\dot{C}CH_2PR_2$ and $R_2\dot{C}CH_2AsR_2$ have isotropic hyperfine coupling constants corresponding to 6.8% s-character. This increase was attributed to a homoconjugation effect involving the lone pair of electrons on phosphorus or arsenic.

In continuation of previous work on radicals derived from trialkylphosphines and -arsines, Lyons and Symons [262] treated the trialkylphosphonium and trialkylarsonium ions (from R_3P and R_3As in sulfuric acid) with γ-radiation from a ^{60}Co source at 77°K. The ESR spectra of the resulting radicals were shown to be characteristic of the radical cations R_3P^+ and R_3As^+. It was concluded that the unpaired electron was in an orbital that had a *p:s* ratio of about 8 and was strongly confined to the central atom. The authors were unable to obtain evidence for Ph_3As^+ radicals from either Ph_3As or Ph_3AsH^+, but only the Ph_2As radicals could be detected. It was concluded that delocalization of the unpaired electron into aromatic rings in the Ph_2As radical is negligibly small.

By means of ESR spectroscopy Furimsky and coworkers [263] have detected the two arsanyl radicals $Ph_3\dot{As}O\text{-}t\text{-}Bu$ and $Ph_2As(O\text{-}t\text{-}Bu)_2$ produced by the photolysis of di-*t*-butyl peroxide and triphenylarsine at temperatures of -100 to -50°. The triphenyl radical was found to have an arsenic hyperfine interaction of 1876 ± 5 MHz. If instead of using triphenylarsine, Ph_2AsOMe, Ph_2AsOEt, or $Ph_2AsO\text{-}t\text{-}Bu$ was used the corresponding radicals $Ph_2\dot{As}(OR)(O\text{-}t\text{-}Bu)$, where R = Me, Et, or *t*-Bu, were obtained. Replacement of one phenyl group in the $Ph_3\dot{As}O\text{-}t\text{-}Bu$ radical by an alkoxy group increased the arsenic hyperfine interaction from 1876 to 2200 MHz. It was concluded that the radicals existed as trigonal bipyramids with the unpaired electron in equatorial and the OR groups in apical positions.

The radicals decomposed principally by α-scission to give a phenyl radical and a trivalent arsenic compound:

$$Ph_3\dot{As}O\text{-}t\text{-}Bu \rightarrow Ph_2AsO\text{-}t\text{-}Bu + Ph\cdot$$

$$Ph_2\dot{As}(OR)(O\text{-}t\text{-}Bu) \rightarrow PhAs(OR)(O\text{-}t\text{-}Bu) + Ph\cdot$$

Rate constants for the decomposition of $Ph_3\dot{As}O\text{-}t\text{-}Bu$ and $Ph_2\dot{As}(O\text{-}t\text{-}Bu)(OR)$ showed that the triphenyl compound was less stable than the diphenyl compound. This was explained by the fact that the triphenyl compound must have one apical phenyl group which would be less stable than an apical O-*t*-Bu group. Alternately the radical $Ph_2\dot{As}(OR)(O\text{-}t\text{-}Bu)$ might undergo Berry pseudorotation with this step being rate-controlling The fact that the $Ph_2\dot{As}(O\text{-}t\text{-}Bu)(OR)$ radicals had different stabilities implied that either the rate constant for pseudorotation or the equatorial As-Ph bond strengths depended on the nature of the R groups.

Although previous attempts to prepare pentamethylarsorane Me_5As have been unsuccessful, Mitschke and Schmidbaur [264] have now successfully prepared this compound from dichlorotrimethylarsonane and two moles of methyllithium in dimethyl ether at -60°. The compound was purified by sublimation at -10° onto a cold finger cooled to -78°. Pentamethylarsonane melts at -7 to -6°. The ^1H NMR spectrum in benzene or toluene showed a sharp singlet at 35° which was not split when the temperature was lowered to -95°. The IR spectrum, however, closely resembled that of Me_5Sb. The IR and Raman spectra of Me_5As were interpreted in terms of a trigonal bipyramid. The compound was remarkably stable in the air and hydrolysed only slowly to Me_4AsOH and methane. With HCl or HF, Me_4AsCl or Me_4AsF, respectively, was obtained.

The use of triphenylarsine as a catalyst for the reaction of alcohols ROH with isoprene to form odorous compounds of the general formula

$ROCH_2C(Me)=CHCH_2CH_2CH(Me)CH=CH_2$ has been described in a patent [265].

Asano and coworkers [266] who have previously reported on the substitution of benzene derivatives with olefins in the presence of palladium(II) salts have now reported on the reaction between Group V aryl compounds Ar_3M, where Ar was usually phenyl and M was N, P, As, Sb, or Bi, and styrene in the presence of palladium(II) acetate. Except for Ph_3N which yielded *trans*-p-diphenylaminostilbene, *trans*-stilbene was always formed. The yield was highest with Ph_3As.

The use of Ph_3As, Ph_3Sb, and Ph_3P in the cooligomerization of esters of the type $CH_2=C(CHRR')CO_2Me$ with butadiene is described in a German patent [267].

A method for the determination of As(V) in organic arsenic compounds without destruction of organic matter has been suggested by Sandhu and coworkers [268]. The compound was dissolved in acetic acid, with the addition of ethanol if necessary, reduced with zinc, and the resulting As(III) titrated iodimetrically.

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