ARSENIC

ANNUAL SURVEY COVERING THE YEAR 1975

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I. Introduction

This review of the organic chemistry of arsenic covers the literature abstracted in volumes 82 and 83 of Chemical Abstracts. Many publications have appeared during this period whose subject matter is concerned with the preparation and characterization of coordination compounds with tertiary arsines, R_3As, as the donor ligands. This area of investigation is more properly treated as a segment of the literature of transition metal chemistry rather than organorsenic chemistry and therefore, is not included in

this review. The preparation of new arsenic containing ligands which form part of that literature and metal complexes with arsenic containing ligands other than tertiary arsines will be described.

II. Reviews and Books

Any books published during 1975 whose content is devoted exclusively to organoarsenic compounds have not come to our attention. Organic arsenicals form part of a review by Wardell [1] on organometallic compounds of As, Sb, and Bi. Metal complexes having arsines as ligands have been reviewed by Cross [2]. A discussion of a number of other soft ligands is also included. The effect of molecular structure on the analytical properties of reagents containing the AsO_3H_2 group has been critically reviewed by Savvin [3].

The very interesting, but poorly understood biochemical interrelationship which exists between arsenic and selenium has been dealt with in a number of recent reviews [4,5,6]. A review by Frost [7] includes a discussion of the use of organoarsenicals in pest control. Diorganylarsinous acid monosaccharide esters are discussed in a review on seleno and thio sugar esters of group VA acids [8].

III. Compounds Having A Metal-Arsenic Bond

Phenylarsine derivatives which possess arsenic-chromium bonds have been reported by Huttner and co-workers [9,10]. The yellow hydride, $(OC)_5CrAs(C_6H_5)H_2$, on treatment with butyllithium, is converted to the orange lithium derivative, $(OC)_5CrAs(C_6H_5)Li_2$. The latter is transformed into the violet phenylarsinidenebis (pentacarbonylchromium), $C_6H_5As[Cr(CO)_5]_2$ by cyclohexyldichloroamine. The arsenic and chromium atoms in the violet compound occupy the three corners

of a triangle with As-Cr bond distances of 2.375 and 2.394 Å. The shortness of these distances is attributed to $Cr_{d\pi}$-$As_{d\pi}$ bonding.

Arsenic to molybdenum bonding has been reported [11] in the compound, $(CF_3)_2AsMn(CO)_5$. The ir and Raman spectra of this compound were measured and a normal coordinate analysis was carried out. The manganese-arsenic stretching frequency was reported at 188 cm^{-1}.

Transphosphination reactions of $(Me_3M)_3P$ and Me_3MPH_2 (M = Si, Ge, Sn) with $HE(CF_3)_2$ or H_2ECF_3 (E = P, As) have been studied by Ansari and Grobe [12]. Derivatives of the type $Me_3ME(CF_3)_2$, $Me_3ME(H)CF_3$ and $(Me_3M)_2ECF_3$ were reported. The reactivities depend on M (Sn > Ge > Si), E(As > P) and the phosphine $[(Me_3M)_3P > (Me_3M)_2PH > Me_3MPH_2]$. Disproportionation of the $Me_3ME(H)CF_3$ gives $(Me_3M)_2ECF_3$ and H_2ECF_3. The M-E bond is cleaved by polar molecules such as HBr. The F_3CE derivatives undergo β-elimination of fluorine to yield Me_3MF and polymers. ^1H and ^{19}F NMR spectral data are reported.

The same investigators [13] have prepared tin-arsenic compounds. The reaction of trimethyltin hydride with tetrakis(trifluoromethyl)diarsine or polytrifluoromethylarsine yields the derivatives $Me_3SnAs(CF_3)_2$, $Me_3SnAs(H)CF_3$ and $(Me_3Sn)_2AsCF_3$.

IV. Compounds Having Arsenic-Nitrogen Bonds

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) reacts with tris(trifluoromethyl) arsine to yield $(CF_3)_2NAs(CF_3)_2$ [14].

The arsenic acid derivative, $K_3[HN = As(NH)_3]$ [15] has been prepared by the reaction between pentaphenylarsane and iminotribenzylarsane with potassium iodide in liquid ammonia. Organylarsanes undergo nucleophilic attack by amide ions at much lower temperatures than the analagous phosphoranes.

The well-known cleavage reaction of the As-N bond by alcohols and thiols has been extended to include the synthesis of oximates [16]. Thus, $As[N(CH_3)_2]_3$ with oximes yields oximates having the formula $[(CH_3)_2N]_2AsONCR_2$, $(CH_3)_2NAs(ONCR_2)_2$ and $As(ONCR_2)_3$. The oximates having As-N bonds react further with alcohols, diols and thiols in the usual manner. Spectral properties, including IR and

^{1}H-NMR data are presented. Koher [17] has prepared bis[bis(dialkylamino)arsino] methanes according to the following reaction

$$H_2C(AsCl_2)_2 + 8HNR_2 \longrightarrow (R_2N)_2AsCH_2As(NR_2)_2 + 4NR_2H_2Cl$$
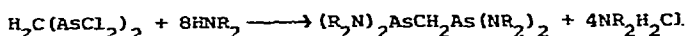
Kaufmann and Kober [18] have utilized methylhalodimethylaminoarsines for the synthesis of methyldihaloarsines bearing two different halogen atoms, as illustrated by the following equation

$$H_3CAs[N(CH_3)_2]X + 2HY \longrightarrow H_3CAsXY + [N(CH_3)_2H_2]Y$$
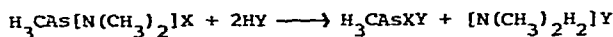
$$X,Y = halogen$$

The same authors [19] have reported on the reaction between aminoarsines and oximes to yield O-(dimethylarsino) oximes. Derivatives having the following structures were prepared:
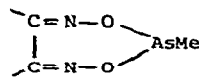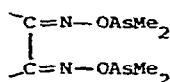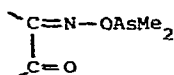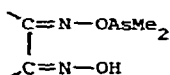
Derivatives which retain an As-N bond are capable of undergoing the usual reactions with acids, a typical example of which is given below.
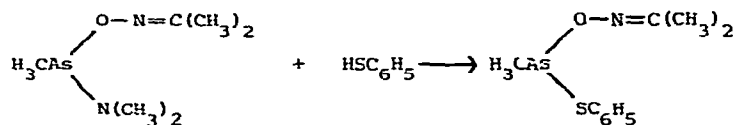
A mechanistic interpretation, and ^{1}H NMR and IR spectral data are presented.

Adler and Kober [20] have prepared trifluoromethylaminoarsines and reported on their physical properties. The dimethylaminoarsine undergoes a transamination reaction with release of dimethylamine.

$$(CF_3)_2AsN(CH_3)_2 + HNR_2 \longrightarrow (CF_3)_2AsNR_2 + HN(CH_3)_2$$
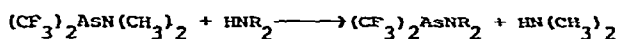
Krommes and Lorberth [21,22] have utilized aminoarsines for the synthesis of diazo arsenic compounds. Dimethylaminodimethylarsine yields, with diazoethyl acetate, $(CH_3)_2AsC(N_2)C(O)OEt$, as a yellow-red relatively air-stable oil. With diazomethane, in the presence of trimethyltin chloride, bis(dimethylarsino)-diazomethane, $[(CH_3)_2As]_2CN_2$ is isolated. Other derivatives were prepared as shown below.
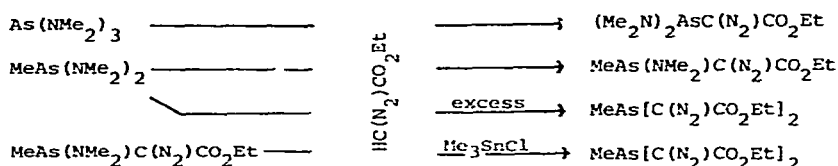
^1H, ^{13}C NMR and IR spectral data are reported for these compounds.

V. Arsines and Polyarsines

Dobbie and Gosling [23] have reported the preparation of 1,2-bis(trifluoromethyl)diarsine, $(CF_3)(H)AsAs(H)(CF_3)$ by the reduction of trifluoromethyldiiodoarsine with mercury using a small amount of HI. In a similar way, they prepared 1,2-bis(methyltrifluoromethyl)diarsine. In MeCN solution, these diarsines are made up of meso and (±)-stereoisomers.

Although tetraphenyldiarsine is well-known and well-characterized, a new and convenient synthesis has been reported [24]. Tetraphenyldiarsine was prepared in 64% yield by the reaction between benzophenone and diphenyllithioarsine according to the following equation

$$2(C_6H_5)_2AsLi + 2(C_6H_5)_2CO \longrightarrow (C_6H_5)_2AsAs(C_6H_5)_2 + 2(C_6H_5)_2CO^- Li^+$$
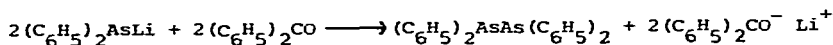
The observation of an EPR signal when a large excess of diphenyllithioarsine was used indicated that benzophenone radical anions were formed.

Iodobis(trifluoromethyl)phosphine reacts with the arsenic compounds Me_3MAsH_2 (M = Si, Sn) to yield the phosphinoarsine, $(CF_3)_2PAsH_2$ [25]. The analogous reaction with $(CF_3)_2AsI$ yields $(CF_3)_2AsAsH_2$, but the compound was

too unstable to be isolated and characterized. The compound, $(CF_3)_2PAsH_2$

was studied in solution below $-40°$ and characterized by mass spectroscopy and

NMR (^1H, ^{19}F, ^{31}P). Both polar [HX, Me_2AsH, Me_2PNMe_2] and non-polar [Br_2,

Me_4As_2] molecules react with cleavage of the P-As bond.

Treatment of cis-$Mo(CO)_4(Me_2PLi)_2$ with Cl_2AsMe yields the interesting

molecule, bis(1,2-dimethylphosphino)-1,2-dimethyldiarsine, $Me_2P-AsMe-AsMe-PMe_2$

[26,27]. Diphenyl-ω-aminoalkylarsines, viz., $(C_6H_5)_2As(CH_2)_nNH_2$(n = 2,3) have

been used as chelating agents [28].

o-Diphenylarsinophenyldiphenylstibine is a white solid, m.p. 166°. It

was prepared [29] in 35% yield by treatment of o-bromophenyldiphenylarsine with

butyllithium followed by the addition of diphenylchlorostibine. o-Phenylenebis-

(diphenylarsine) [30] was obtained by adding lithium diphenylarsenide to o-bromo-

phenyldiphenylarsine in tetrahydrofuran under nitrogen. The arsine, m.p. 199°

was obtained in 54% yield. Chow and McAuliffe [31] prepared the novel open-

chain tetratertiary arsine 1,3-propanebis(3-dimethylarsinopropylphenylarsine)

according to scheme 1. The same laboratory [32] reported the synthesis of the

following ligands:

Scheme 1
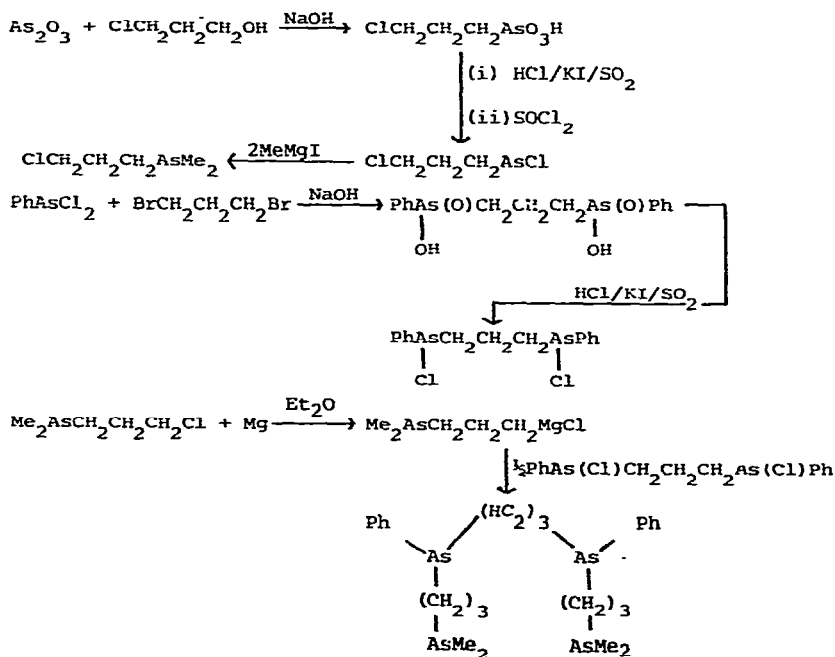
1-Chloro-2-diphenylarsinoethane, $ClCH_2CH_2As(C_6H_5)_2$, b.p. 144-148/2 torr;
and 2-diphenylarsinodiphenylphosphinoethane, $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$,
m.p. 120°. Tris(o-dimethylarsinophenyl)bismuthine [33] (bitas) may
function as both a tridentate and tetradentate ligand in $[Ni_2(bitas)_3]^{4+}$.

Bosnich and co-workers [34] have prepared two linear quadridentate
tetra(tertiary arsines): one has three o-phenylene linkages, o-phenylenebis-
(o-dimethylarsino-phenylmethylarsine) and the other has a central o-phenylene
linkage and two terminal trimethylene arms, o-phenylenebis(dimethylarsino-
γ-propylmethylarsine). The racemic and meso forms of both arsines were
separated and identified by way of their cobalt(III) complexes. The
synthesis of o-phenylenebis(methylphenylarsine) by the reaction between
o-dichlorobenzene and sodium methylphenylarsenide in tetrahydrofuran has
been described by Henrick and Wild [35]. The diastereoisomers, meso-(RS)
and racemic-(RR,SS) forms, were separated by crystallization and conversion
to the benzylarsonium salts. Further identification of the diastereoisomers
was effected via the coordination compounds formed with Pt(I). In
particular, good use was made of the chemical shifts and coupling constants
J(Pt-H). For example, in complexes of the type $[PtX(R)(Me_2)L_2]$ (X=halide,
R=alkyl and L=tertiary arsine), J(Pt-H) lies within the ranges 69-73
(trans-X), 60-66.5 (trans-As), and ca. 44Hz (trans-methyl).

Cullen and Mihichuk [36] studied the reaction of bis(trifluoromethyl)-
acetylene with sym-dimethyldiphenyldiarsine and obtained almost equal
amounts of cis- and trans-$(C_6H_5)(CH_3)AsC(CF_3)=C(CF_3)As(CH_3)(C_6H_5)$, (L-L).
The racemic form of the cis-isomer is obtained as a pure solid while the
meso form of the cis-isomer is an oil. Both the racemic and meso isomers
give, with iron pentacarbonyl, the complexes $(L-L)Fe(CO)_3$ and $(L-L)Fe_2(CO)_6$.
The cis-geometry of the isomer was confirmed from the properties of the
iron carbonyl complexes.

Kepert and Trigwell [37] in their investigations of the influence
of incorporating fluorine atoms into ditertiary arsines on their
reactions with metal halides have prepared several fluorine-containing
ligands. They are the fluoroalicyclic-bridged ligands, 1,2-bis(dimethyl-

arsino)-3,4,4-tetrafluorocyclobutene and 1,2-bis-(dimethylarsino)-3,3,4,4,5,5-hexafluorocyclopentene and the fluoroaromatic-bridged ligands, 1,2-bis(dimethylarsino)-3-fluorobenzene and 1,2-bis(dimethylarsino)-4-fluorobenzene. Clark and Stockwell [38] in their investigations on complexes of group VI hexacarbonyls with group V ligands having an olefinic side chain have prepared $H_2C=CHCH_2CH_2AsMe_2$.

The thermodynamic functions of gaseous trimethylarsine have been calculated in range 298-1200°K by Russian investigators [39]. Methods of statistical thermodynamics in terms of the rigid rotator-harmonic oscillator approximation were employed. The barrier to the internal rotation of gaseous trimethylarsine was found to be 1.5 ± 0.5 kcal mole^{-1}.

$C_p^o{}_{298.15} = 26.33$ cal.mole^{-1}deg^{-1}; $S^o{}_{298.15} = 83.42$ cal mole^{-1};

$H^o{}_{298.15} - H^o_o = 5269$ cal mole^{-1}.

VI. Compounds Containing Arsenic-Oxygen Bonds

Chernokal'skii and co-workers [40] studied the reactions of dialkyl- and alkylphenylarsinous acid esters with alkyl halides. The products were quaternary arsonium salts and esters of arsonous acid.

$$2RR'AsOR'' + RX \longrightarrow [R_3AsR']X + R'As(OR'')_2$$
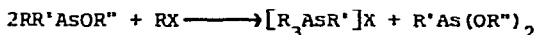
These authors reported on the IR spectra of the arsonous acid esters. In a kinetic study of the reaction of diethylethoxyarsine with alkyl halides [41], the reaction with ethyl iodide in acetone was found to be first order with respect to each reactant. In this study, the rates and activation energy and entropy were reported.

Based on thermogravimetric and infrared studies, Indian workers [42] have concluded that the structures of "o-benzarsenious oxide monohydrate" and its anhydride are those shown below.
Shagidullin [43], based on IR spectral studies, has offered an explanation for the transformations observed in the IR spectra of $(MeO)_3AsO$ and $(EtO)_3AsO$ when these compounds are allowed to cool and crystallize. The changes
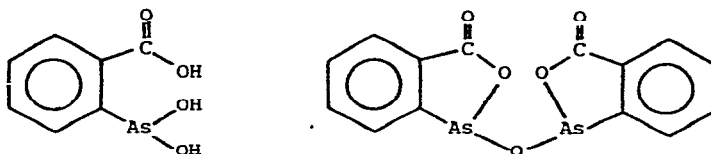
observed are attributed to dipole-dipole associations of the following

kind with the most probable value for n being one.
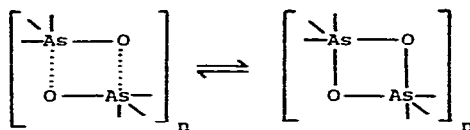
Garner and Hughes [44] have prepared and studied the properties of

arsenic tris(trifluoroacetate). The compound was prepared by the reaction

between arsenic trichloride and silver trifluoroacetate in methylene chloride.

The compound was obtained as an extremely hygroscopic solid melting at

45.5-4.6°. The molecule readily adds a mole of boron tribromide to form

$(CF_3CO_2)_3As \cdot BBr_3$.

Argentine workers [45] have studied the effect of butylarsonate concen-

tration on the yield of n-butylarsonic acid in the Meyer reaction. They

found that the inhibition period of about 70 hrs. could be reduced to

just a few hours when an initial butylarsonate concentration of 2.57M

was used. At lower initial concentration of butylarsonate the inhibition

period was found to be proportionally longer. The catalytic effect of

butylarsonate is attributed, in part, to its function in assisting in

the mixing of the otherwise immiscible phases.

The acid strengths of several phenylarsonic acids in cyclohexanol

and butyl alcohols have been determined by Gureeva and co-workers [46].

The strength of phenylarsonic acid diminishes on going from water to

alcohols, e.g., the pK of phenylarsonic acid is 3.59 in water and 9.81

in tert-butyl alcohol. The trend in pK values was correlated with the

nature of the substituent group on the aromatic ring as well as the ability

of the molecule to undergo intermolecular association. The phosphonic

acids are stronger than their arsenic analogues and this is attributed

to the greater effect of $d\pi$-$p\pi$ interaction in the phosphorus compounds. Some preliminary crystallographic data have been reported for p-amino-phenylarsonic acid, o-aminophenylarsonic acid, and 4-hydroxyphenylarsonic acid [47, 48, 49].

Heteropoly complexes prepared from sodium molybdate and arsinic acids have been reported by Barkigia et al. [50]. A compact and symmetrical anion is formed which consists of a ring of four alternately face- and edge-shared MoO_6 octahedra capped by the R_2AsO_2 tetrahedra. Bond distances and bond angles are reported.

Triorganylarsine oxides have served as coordinating agents for the preparation of a number of metal ion complexes. Brnicevic [51] has prepared complexes of the composition $M/NbO(C_2O_4)_2[(C_6H_5)_3AsO]_2$ where M is NH_4^+ or an alkali metal ion. Peroxo complexes of the type $\{M(O-O)F_3[(C_6H_5)_3AsO]_2\}$, where M is Nb, Ta or WO have been reported [52]. The ligand, 1,2-ethylenebis(diphenylarsine) oxide has been used as a coordinating agent in the preparation of a number of complexes of La(III), Nd(III) and Sm(III) [53].

The electrochemical oxidation of triphenylarsine in wet acetonitrile at platinum electrodes has been studied by Italian workers [54]. Hydroxytri-phenylarsonium chloride is formed by the reaction of triphenylarsine with chlorine radicals generated at the anode surface or the direct oxidation of triphenylarsine. In all of the electrochemical processes, a hydrolytic reaction involving the water in the solvent is involved. When tetrafluo-borate was used as the supporting electrolyte, the formation of $(C_6H_5)_3AsOBF_3$ is attributed to the elimination of HF from hydroxytriphenylarsonium tetrafluoroborate. When perchlorates were used as the supporting electro-lytes, $[(C_6H_5)_3AsO]_2HClO_4$ was obtained by the partial reduction of $(C_6H_5)_3As(OH)ClO_4$ formed by the anodic oxidation of triphenylarsine.

The dynamic stereochemistry of oxyarsoranes has been studied by Russian and Scandinavian investigators [55, 56]. In compounds of the type shown below,
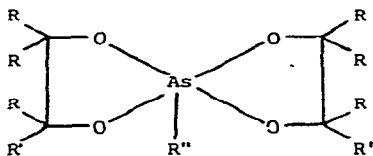
the temperature dependence of the PMR spectra indicate the presence of a

rapid exchange process. In the case of the derivatives in which R = R' = CH_3

and R" = $CH_2C_6H_5$ or $p\text{-}O_2NC_6H_4$, in bromobenzene at room temperature, only

two methyl proton resonances are observed. The methyl resonances broaden

and merge into a singlet with rise in temperature. At -100°, a poorly

resolved set of four lines is observed. When R" is benzyl, the benzyl

protons remain unchanged with temperature which suggests that the exchange

process is intramolecular.

Dale and Froyen [56] studied the exchange reactions of a series of

acyclic oxyarsoranes with pinacol and 2,2-dimethyl-1,3-propanediol.

The formation of five- or six-membered cyclic oxyarsoranes generally

occurred. The quantitative formation of a spiroarsorane took place when

the diol compound was mixed with the arsorane, $R\text{-}As(OCH_3)_4$, (R = OCH_3,

CH_3, C_6H_5), in a 2:1 ratio. At molar ratios of 1:1 the monocyclic

arsorane formed quantitatively only in the case where the diol is pinacol

and R = OCH_3. When R = CH_3 or C_6H_5 a mixture of products including the

spiro and perhaps the monocyclic compounds was obtained. The bis-ring

compound appears to be thermodynamically more stable than the mono-ring

whether the ring is five- or six-membered. The spiroarsoranes derived

from pinacol are generally more stable than those derived from 2,2-dimethyl-1,

3-propanediol. Several isolatable oxyarsoranes were studied by variable

temperature NMR and the results interpreted in terms of a pseudorotation

process. The pseudorotations were found to be similar to those undergone by

analagous compounds of phosphorus.

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

Heating the enantiomers of o-, m-, and p-(ethyl-p-tolylarsino)anilines

with sulfur in dry benzene converted them to the arsine sulfides. Analyses
and IR spectra were reported [57]. Triphenylarsine sulfide reacts with
dimethyl sulfate in methylene chloride to yield the (methylthio)triphenyl-
arsonium salt, $[(C_6H_5)_3AsSCH_3]CH_3SO_4$. Stable (alkylthio)arsonium salts
are also formed when tricyclohexylarsine sulfide is caused to react with
methyl iodide or triethyloxonium tetrafluoroborate in methylene chloride
at room temperature [58, 59]. Phenyl-p-tolylarsinothioic acid, $C_6H_5(p\text{-tol})$
As(S)OH has been synthesized [60] and its resolution into optically active
enantiomers has been attempted. Racemic phenyl-p-tolylarsinothioic acid
has been prepared according to the following reaction scheme:

$$C_6H_5As(ONa)_2 \xrightarrow[\text{HCl}]{\text{p-ToIN}_2\text{Cl}} C_6H_5(p\text{-Tol})As(O)OH \xrightarrow{\text{PCl}_5}$$

$$C_6H_5(p\text{-Tol})As(O)Cl \xrightarrow[\text{H}_2\text{S, HCl}]{\text{HN(Et)}_2} C_6H_5(p\text{-Tol})As(S)OH$$
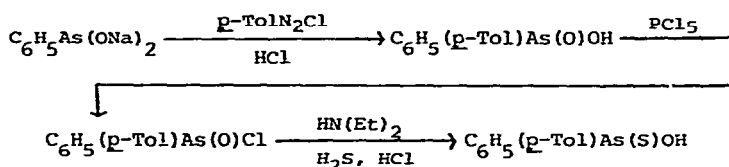
Zingaro and co-workers have continued their investigations on thio
and seleno sugar esters of diorganylarsinous acids. This work has been
the subject of a recent review [8]. In 1975 [61] the syntheses of 6-thio
and 6-seleno-β-D-glucose esters of dimethylarsinous acid were described.
In order to prepare the 6-seleno derivative it was necessary to use
the stronger nucleophile, N,N-dimethylselenourea, in place of selenourea
to effect the conversion of 6-iodo-β-D-glucopyranose to the pseudoureide.

VIII. Compounds Containing Arsenic-Halogen (Halogenoid) Bonds

Dimethylchloroarsine forms the adducts $(CH_3)_2AsCl \cdot (TU)_n$ (n = 1,2)
with thiourea, TU.

The IR spectrum of the bis(thiourea) complex shows no As-Cl stretching
vibration. According to an x-ray structural analysis [62], the compound
is ionic and has the formula $[(CH_3)_2AsSC(NH_2)_2]^+Cl^- \cdot SC(NH_2)_2$. The sulfur
atom of the thiourea group has displaced the chlorine atom. The As-S
distance is only slightly longer than that of a "normal" As-S single bond.

Alkyldiiodoarsines $(C_nH_{2n+1})AsI_2$ (n = 1, 3, 4, 14, 15, 16, C_6H_5) and dialkyliodoarsines $(C_nH_{2n+1})_2AsI_2$ (n = 1, 8, 10, 12, 16) have been prepared from the appropriate organoarsenic acids by their reaction with concentrated hydriodic acid [63]. Trichloroisocyanuric acid reacts with $AsCl_3$ to form $Cl_2As(N_3C_3O_3Cl_2)$ [64]. Lithium cyclopentadienides react with chloroarsines to form cyclopentadienylarsines. The following derivatives were reported [65]:

$$H_3C-C_5H_4-As(CH_3)_2, \quad H_3C-C_5H_4-As(CH_3)Cl, \quad H_3C[(CH_3)_3Si]C_5H_3As(CH_3)_2$$

$$\text{and } [(CH_3)_3Si]_2C_5H_3As(CH_3)_2.$$
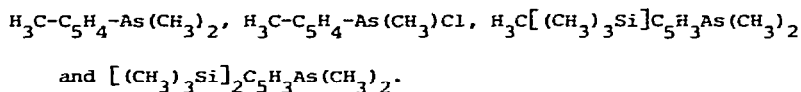
Mass spectral and ^{1}H NMR data for these compounds were reported.

Kober and Rühl [66] investigated the reactions of dimethylarsinous acid glycol esters with arsenic halides and other reagents. Some of the reactions studied are shown below.
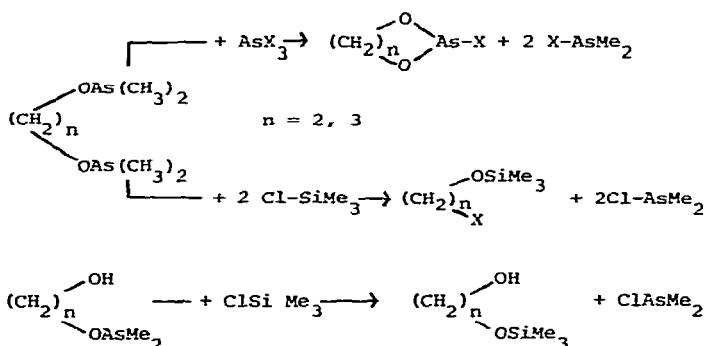
Other arsenic-bearing derivatives of the types shown below were also prepared.
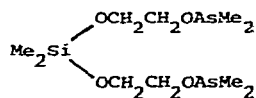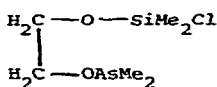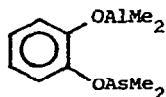
The compound, was proposed as an intermediate in the

reaction between trimethylaluminum and dimethylarsinous acid glycol esters, but only polymers were isolated. ^{1}H NMR spectra of all compounds prepared were reported. Russian workers [67] synthesized some heteroorganic compounds (_1_, _2_).
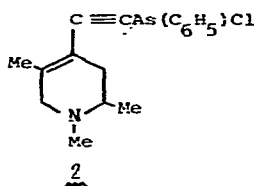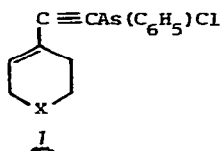
Chlorotrimethylarsonium chloride reacts with dimethylchloroindium in methylene chloride to yield tetramethylarsonium methyltrichloroindate, $[(CH_3)_4As]^+$ $[CH_3InCl_3]^-$ [68]. The A_1 $\nu_s(AsC_4)$ vibration was reported at 589 cm^{-1}.

Ansari and Grobe [69] reported a simplified and efficient synthesis for trifluoromethylarsines. The reaction of $(CF_3)_2AsI$ with $(CH_3)_3SnH$ gives F_3CAsH_2 when treated with two moles of the tin hydride. Ionov et al. [70] prepared cyanoisobutyl-p-tolylarsine by the reaction between the diorganylchloroarsine and KCN in acetone. Hydrolysis and permanganate oxidation gave the interesting carboxylic acid, $(\underline{p}-HO_2CC_6H_4)(\underline{iso}-C_4H_9)As(O)COOH$. In this work, racemic benzylcyanoisobutyl-p-tolylarsonium bromide was resolved into the dextro- and levo-forms _via_ the diastereomeric dibenzoyltartrates.

IX. Triorganyl Arsines

This section covers compounds containing three carbon to arsenic bonds which are not easily classified in the other sections of this review.

A. Asymmetric Triorganylarsines

Russian workers have been active in the synthesis and resolution of asymmetric arsines. The synthesis of a series of alkylarylaminoarsines

has been reported by Yambushev and co-workers [71]. *In their approach to the synthesis of (aminoaryl)arsines*, they made considerable use of the lithium exchange reaction. When NH proton(s) are present on the aryl substituent, an excess of organolithium compound must be used. Because the aryllithium is much more reactive than the aminolithium, condensation with the halogenarsine proceeds in the desired direction. They prepared a series of derivatives as described by the following equation.

$$RArAsCl + LiC_6H_4NLi_2 \longrightarrow RArAsC_6H_4NLi_2 \xrightarrow{\text{hydrolysis}} RArAsC_6H_4NH_2$$
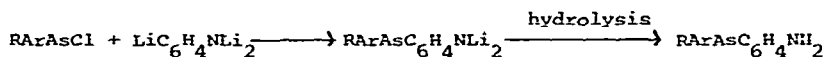
Asymmetric diorganyl(carboxy)arsines have been characterized by Gatilov et al. [72]. The most efficient method for the preparation of these derivatives involved the reaction of chloroformic esters with arseno-Grignard reagents.

$$RArAsH + R^1MgX \longrightarrow RArAsMgX + R^1H\uparrow$$

$$RArAsMgX + ClCOOR^2 \longrightarrow RArAsCOOR^2$$
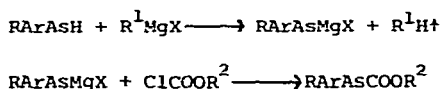
Yields of the arsines were reported to be about 80%. They are colorless liquids having a characteristic odor. They readily hydrolyze on exposure to atmospheric moisture.

Asymmetric diorganyl(carboxy)arsine oxides have been synthesized by Ionov et al. [73]. One synthetic approach involves the hydrolysis of a nitrile group bonded directly to arsenic.

$$RArAsR' + BrCN \xrightarrow{140 - 150^0} RArAsCN + R'Br$$

$$RArAsCN \xrightarrow{H_2O_2} RArAs(O)COOH$$

$$RArAs(O)COOH \xrightarrow[CH_3COOH]{SO_2, \ H_3PO_2} RArAsCOOH$$
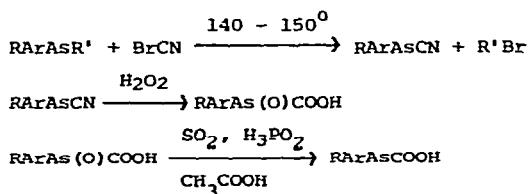
Other carboxylic acid derivatives in which two aryl groups are bonded to arsenic were prepared from diarylalkylarsines. Sodium in liquid ammonia cleaves the alkyl-arsenic bond forming sodium diarylarsenide. The latter can then be reacted with a haloalkylcarboxylic acid derivative.

$$ArAr'AsNa + X(CH_2)_nNC(O)Y \longrightarrow ArAr'As(CH_2)_nC(O)Y$$

$$X = halogen \qquad Y = OH, OR, NH_2$$
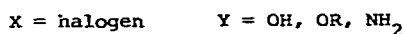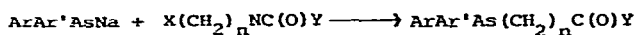
A series of ten derivatives was prepared.

Quinine was found to be an effective reagent for the resolution of ethylphenyl(carboxy)arsine. The diastereoisomeric quinine salts were found to possess quite different solubilities in methanol and chloroform which made possible their separation as diastereoisomers [74]. The oxidative addition of sulfur to (+)-ethylphenylarsinoformic acid converts it to the dextrorotatory arsine sulfide.

For the preparation of (aminophenyl)ethyltolylarsines, the amino group has been protected via its conversion to the N,N-bis(trimethylsilyl) derivative [75].

$$BrC_6H_4NH_2 + 2EtMgBr \longrightarrow BrC_6H_4N(MgBr)_2$$

$$BrC_6H_4N(MgBr)_2 + 2Me_3SiCl \longrightarrow BrC_6H_4N(SiMe_3)_2$$
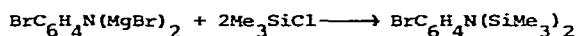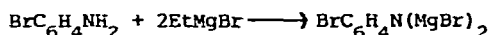
The trimethylsilyl protected aminobromobenzene is then converted to the arsino derivative in the usual manner

$$(Me_3Si)_2NC_6H_4MgBr + CH_3C_6H_4EtAsCl \longrightarrow CH_3C_6H_4EtAsC_6H_4N(SiMe_3)_2$$
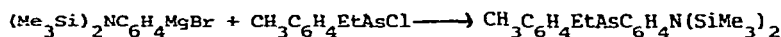
The trimethylsilyl groups are readily removed by mild acid hydrolysis.

The resolution of o-, m-, and p-(ethyl-o-tolylarsino)anilines into their optically active isomers by way of their tartrates has been reported by Russian workers [76].

Studies on acylarsines reveal that in compounds of the type MeCOAsR$_2$, the protons of the R substituents are magnetically equivalent over a wide temperature range [77]. This rules out the possibility of R$_2$As being located in the plane of the MeCO group. The high pyramidal stability of As in acylarsines means that optically active acylarsines with a chiral arsenic atom can be synthesized.

Arsines and arsonium salts containing one or two acetylenic bonds have been the subject of a recent ^{1}H NMR study [78]. As the

positive charge on the arsenic atom increases the proton signals of the substituent alkyl groups are shifted downfield. The non-equivalence in the protons of methyl and methylene groups, $\Delta\delta = \delta(CH_2) - \delta(CH_3)$ is magnified (increase in $\Delta\delta$) as one goes from 3-coordinate to 4-coordinate arsenic. Thus, in triethylarsine, $\Delta\delta = 0$, but in $[(C_2H_5)_4As]^+$, $\Delta\delta = 1.75$. Based on NMR data, the decrease in electron density on an arsenic atom, upon replacing an ethyl group by an acetylenic group is associated with the "electronegative effect and diamagnetic susceptibility of the $-C\equiv C$ bond".

B. Other Aspects Of Triorganylarsines

Dimethyl-σ-cyclopentadienylarsine has been prepared by Krommes and Lorberth [79] by the reaction between dimethylaminodimethylarsine and cyclopentadiene in the presence of Me_3SnCl. Mass spectral and ^1H NMR data are presented for this compound which is a pale yellow oil, b.p. $39°/4$ torr. Attempts to prepare $MeAscp_2$ from $MeAs[N(CH_3)_2]_2$ using a similar reaction were unsuccessful.

Trimethylarsine forms 1:1 addition compounds with BBr_3 and BI_3. The adducts are stable indefinitely in the absence of moisture. $(CH_3)_3As \cdot BI_3$ in chloroform decomposes to give what is probably $[(CH_3)_3AsI]^+I^-$. Mente and Mills [80] performed a number of physical measurements on $Me_3As \cdot BX_3$ adducts. The enthalpies of formation (kcal/mole) were as follows: $X = F$, -20.4; $X = Cl$, -46.2; $X = Br$, -81.2; $X = H$, -49.6. Shifts in $\nu(As-C)$ were relatively small, of the order of 10-20 cm^{-1}. Mass spectral data were also recorded.

Pahil and Sharma [81] reported that As(III) in organoarsenicals was easily determined by iodimetric titration. The compound is dissolved in methanol, heated under reflux, and titrated by iodine in methanol.

The mixture, Me_3Sb, Me_3As, $(CH_3)_2Se$ and $(CH_3)_4Sn$ was subjected to gas chromatographic separation. Using water-free helium as the carrier gas and dodecyl benzenesulfonate as the stationary phase, good separations and quantitative estimates were obtained [82].

X. Arsonium Compounds, Arsenic Ylides and Arsanes

Methylenetriphenylarsane, $(C_6H_5)_3As=CH_2$ has been isolated by Yamamoto and Schmidbaur [83]. Treatment of $[(C_6H_5)_3AsMe]Br$ with $NaNH_2$ in dry tetrahydrofuran followed by filtration and evaporation of the solvent yields yellow crystals of the compound, m.p. 74°. It is thermally unstable, both in the solid state and in solution. Deprotonation of the methyl group leads to only a slight reduction in $^1J(CH)$, from 142.0 to 136.7 Hz in contrast to the large increase observed upon deprotonation of the corresponding phosphorus compound. This is interpreted in terms of greatly reduced π-bonding in the arsenic compound and a probable pseudo-tetrahedral geometry. Ferguson and Rendle [84] determined the crystal structure of 1-acetyl-2,3,4-triphenyl-5-(triphenylarsonium) cyclopenta-dienide. They considered the relative contributions of the canonical forms shown below. The bond lengths within the five-membered ring fall
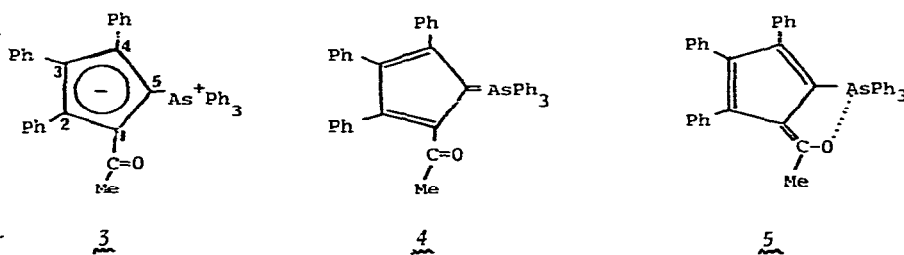
into the categories: C(1)-C(5) and C(3)-C(4), mean 1.406; C(2)-C(3) and C(4)-C(5), mean 1.4222; and C(1)-C(2), 1.445Å. The As···O distance, 2.770(3)Å is considerably less than the sum of the appropriate van der Waals radii (3.40Å), but greater than the expected As-O covalent bond distance. Based upon the bond lengths, the authors speculate that the relative population densities of canonical forms are 20-30% 3, and 30-35% 4, and 40-45% 5.

The crystal structure of the closely related molecule, triphenyl-(2-acetyl-3,4,5-triphenylcyclopenta-2,4-dienyl)arsonium perchlorate has also been reported [85]. It was concluded that there is no delocali-zation between the arsonium moiety and the cyclopentadienide system.

The geometry about the arsenic is that of a slightly distorted tetrahedron [As^+····O(Ac) 3.100(11)$\mathring{A}$]; As^+—C(sp^3) is 1.963±0.013$\mathring{A}$, and mean As^+—C(Ph)1.908±0.007$\mathring{A}$. The arsenic-carbon distance does not differ from the sums of the relevant single covalent bond radii (1.98$\mathring{A}$).

A number of synthetic studies on arsenic ylides have been reported. Freeman and Lloyd [86] have found copper-bronze to be an effective catalyst for the preparation of phenyl-substituted cyclopentadienylides by a carbene type of decomposition of diazocyclopentadienes. Of interest was the formation of triphenylarsonium 2,4-diphenylcyclopentadienylide when 2,5-diphenyldiazocyclopentadiene decomposed thermally in the presence of triphenylarsine.
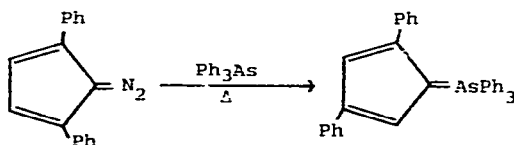
The mechanism of the rearrangement is unknown, but the authors speculate on a hydrogen atom migration. Triphenylarsonium 2,4-diphenylcyclopentadienylide was prepared also by condensation of triphenylarsine oxide with 1,4-diphenylcyclopentadiene in triethylamine in the presence of P_2O_5. An attack by triphenylacetoxyarsonium ion on the 1,3-diphenylcyclopentadienide anion is assumed. Attempts to prepare the hydrobromide of triphenylarsonium 2,3,4-triphenylcyclopentadiene with triphenylarsine in a melt were unsuccessful. This method has been used successfully for the preparation of the phosphonium analog.

The semi-stabilized arsonium ylides, o-nitrobenzylidenetriphenylarsane and m-nitrobenzylidenetriphenylarsane were prepared by Indian workers [87]. Treatment of these arsanes with a variety of carbonyl compounds yielded trans-olefins exclusively; epoxides were never isolated. Similar results were reported [88] when the ylides, p-bromo- and p-iodobenzylidenetriphenylarsane were treated with a variety of carbonyl compounds.

Vinyltriphenylarsonium bromide was prepared by treating β-chloro-

ethyltriphenylarsonium bromide with triethylammonium ion in methylene chloride or with aqueous silver oxide [89]. A series of derivatives were prepared by the β-addition of alkanols, thiols, amines and active methylene species. The derivatives were of the type $[(C_6H_5)_3AsCH_2CH_2X]Y$ where X is OR, NHR, NR_2, SR, $C(CN)_2$ and Y is ClO_4^-, $B(C_6H_5)_4^-$, or Br^-. Arsonium ylides having the formulas $(C_6H_5)_3As=CHC_6H_4X$, where X is I or Br were reported by Gupta and Tewari [90]. These were caused to react with acyl chlorides to form carbonyl stabilized arsonium ylides of the type $(C_6H_5)_3As=C[C(O)R](C_6H_4X)$.

A most interesting transylidation reaction has been discovered by Schmidbaur and Richter [91]. The reaction between methylenetrimethylarsane and cuprous chloride or silver chloride-trimethylarsine in a 2:1 molar ratio yields copper or silver dimethylarsonium bis(methylide)dimers. Coupling constants for $J(^{107,109}Ag-C-^1H)$ were measured. The compounds were formulated as

$$H_3C \diagdown \diagup CH_2 {\rm —} M {\rm —} CH_2 \diagdown \diagup CH_3 \qquad M = Ag, Cu$$
$$H_3C \diagup As \diagdown CH_2 {\rm —} M {\rm —} CH_2 \diagup As \diagdown CH_3$$

Lumbroso and co-workers [92] measured the electric dipole moments in benzene of seven acylmethylenetriphenylarsanes. The lowest measured value was 5.40D for $C_6H_5C(O)CH=As(C_6H_5)_3$ and the highest was 9.33D for $\underline{p}-NO_2C_6H_4C(O)CH=As(C_6H_5)_3$. Because of these relatively high values, the molecules were assumed to possess an (As,O)-<u>trans</u> conformation.

$$R \diagdown \underset{|}{C} \diagup \overset{\overset{O}{\parallel}}{C} \diagdown O \diagup R$$
$$As(C_6H_5)_3$$

(As, O)-<u>trans</u> form

The moments of some triphenylphenyliminoarsane derivatives were also measured. For triphenyl(<u>p</u>-nitrophenylimino)arsane, the electric dipole moment was measured as 8.41D.

The tetraphenylarsonium ion has found widespread application in the

preparation and characterization of complex metal anions. Only a few examples will be cited here. The crystal and molecular structure of tetraphenylarsonium tris(benzenedithiolato)tantalate(V) has been reported by Martin and Takats [93]; Koepke and co-workers [94] have synthesized and characterized tetraphenylarsonium tri-μ-hydrido-dodecacarbonyltetra-ruthenate; tetraphenylarsonium chloromolybdates have also been reported [95].

Tetramethylmethoxyarsane has been prepared from the silyl-substituted arsenic ylide $(CH_3)_3As=CHSi(CH_3)_3$ by treatment with methanol. The last step in the synthesis is the following [96]:

$$(CH_3)_3As=CH_2 \xrightarrow{\text{MeOH}} (CH_3)_4AsOCH_3$$
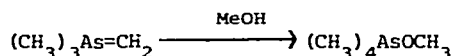
^1H and ^{13}C NMR data were reported.

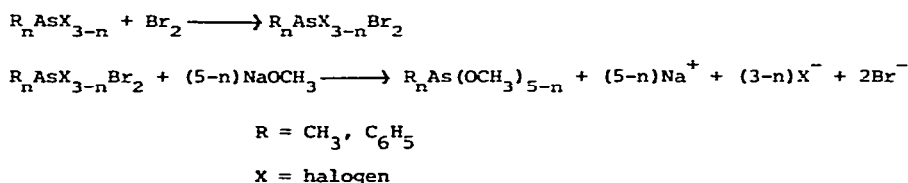Tetramethylaminooxyarsanes have been reported by Ott, Weidlein and Mischke [97]. The derivatives, $(CH_3)_4As-ONH_2$ and $(CH_3)_4As\cdot_\jmath-N(CH_3)_2$ decompose explosively on contact with chlorinated hydrocarbons; $(CH_3)_4As-O-N=C(CH_3)_2$ and $(CH_3)_4As-O-N=CHCH_3$ are air and moisture sensitive and exist as syn- and anti-isomers. ^1H NMR chemical shifts and IR data were reported for these compounds.

Organyl(alkoxy)arsanes of the type $As(OCH_3)_5$, $H_3CAs(OCH_3)_4$, $C_6H_5As(OCH_3)_4$, $(H_3C)_2As(OCH_3)_3$, $(C_6H_5)_2As(OCH_3)_3$, and $(C_6H_5)_3As(OCH_3)_2$ were prepared according to the following general reactions [98]:

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

$$R_nAsX_{3-n}Br_2 + (5-n)NaOCH_3 \longrightarrow R_nAs(OCH_3)_{5-n} + (5-n)Na^+ + (3-n)X^- + 2Br^-$$

$$R = CH_3, C_6H_5$$

$$X = halogen$$

The trigonal bipyramidal geometry of these molecules and the positions occupied by the substituent groups were established by temperature dependent NMR spectroscopy. In $RAs(OCH_3)_4$ the methoxy groups are equivalent down to -100° which is consistent with a very low activation energy for the pseudorotation process. Among the derivatives prepared only $(C_6H_5)_2As(OCH_3)_3$

showed qualititative difference in the NMR spectrum at different temper-

atures. At room temperature the OCH_3 resonance is broad and at 40° is

split into two signals ($\delta3.02$ and 3.98) in a ratio of 2:1. At 50° a

sharp singlet at 3.36 appears. The low temperature spectrum is in agree-

ment with the structure predicted from the electronegativity rule--viz.,

that the two phenyl groups occupy equatorial positions. This geometry

leads to a greater shielding of the equatorial OCH_3 group. The signal

of higher intensity is at the higher field, as expected. From the

coalescence temperature and the chemical shift difference between the

two methoxy signals, 58Hz, the free energy of activation at the coalescence

temperature was estimated at 14.4 kcal. mol^{-1}.

XI. Arsenic Heterocycles

The arsabenzenes have been the subject of considerable investigation.

Märkl and his co-workers have been active in the synthesis of arsabenzenes

bearing functional groups. Recent reports have described the syntheses

of arsabenzene-4-carbaldehyde [99, 100], 4-alkoxyarsabenzenes [101], and

4-hydroxyarsabenzene [102]. The starting compound for the preparation

of the 4-carbaldehyde was 1-chloro-4-alkoxy-4-(diethoxymethyl)-1,4-

dihydroarsabenzene 6.   Treatment of 6 with R_3SnH converts the As-Cl

to an As-H bond 7.   Loss of alkanol from 7 gives 4-diethoxymethyl-

arsabenzene which, on treatment with acid, is converted to arsabenzene-4-

carbaldehyde. The thermal decomposition of 6 brought about the loss

of $(EtO)_2CHCl$ and the formation of the 4-alkoxyarsabenzene. For the

preparation of 4-hydroxyarsabenzene, the starting material was

1-chloro-4-acetoxy-1,4-acetoxy-1,4-dihydroarsabenzene 8. Loss

of HCl from two moles of 8 occurs spontaneously to give 4-acetoxyarsa-

benzene. The latter is converted to "arsaphenol" by treatment with sodium

hydroxide in aqueous methanol. Spectral data, including IR and ^{1}H NMR

shifts are reported.

The synthesis of methyl substituted arsabenzenes has been described

[103]. The tin isomers formed by the reaction of dibutyltin dihydride with 1,4-hexadiyne were heated with arsenic trichloride. This gave a 43% yield of 2-methylarsabenzene. Ashe and Chan [104] measured the dipole moments of 4-methylpyridine (2.57D), 4-methylphosphabenzene (1.77±0.12D), and 4-methylarsabenzene (1.50±0.11D) as well as pyridine (2.20D), phosphabenzene (1.46±0.04D), and arsabenzene (1.02±0.02D). In all three cases the negative end of the dipole is at the hetero atom. The major contribution to the pyridine dipole is the difference between the very electropositive α-carbon atoms and the electronegative nitrogen. In the case of phosphabenzene and arsabenzene the major contribution to the dipole moment comes from the large negative charge on the α-carbon atoms and a large positive charge on the β-carbon atoms.

In Table I are listed bond distances and bond angles which have

TABLE I

Bond Distances and Bond Angles in Arsabenzene
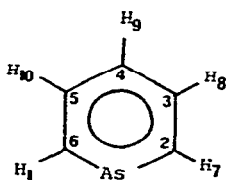
$d[C_2(orC_6)-As]$	1.850(3)Å
$d(C_2-C_3)$	1.390(32)
$d(C_3-C_4)$	1.401(32)
$d(C-H)ave$	1.120(15)
$\angle C_6AsC_2$	97.3°(1.7)
$\angle AsC_2C_3$	125.1°(2.8)
$\angle C_2C_3C_4$	124.2°(2.9)
$\angle C_3C_4C_5$	124.2°(2.9)
$\angle AsC_2H_7$	116.1°(2.7)
$\angle C_2C_3H_8$	118.6°(4.9)

recently been measured in an electron diffraction study of arsabenzene
[105]. The carbon-carbon bond lengths (or their mean value) fall within
the range associated with aromatic C-C bond lengths. The C-As bond
length also indicates considerable double bond character. The CAsC
bond angle (97.3° is small compared with benzene (120°), pyridine
$\nmid$CNC(116.83°), and phosphabenzene $\nmid$CPC(101.12°). This is to be expected
in view of the increasing carbon to hetero atom bond length.

Ab initio calculations have been performed for pyridine, phospha-
benzene and arsabenzene [105]. In pyridine, the overall sigma charge
is negative due largely to electron migration from the adjacent CH
groups. In phospha- and arsabenzene the heteroatoms are overall σ-
election donors to the adjacent CH groups. The relative changes in
population are greater in going from pyridine to phosphabenzene than
from phospha- to arsabenzene.

The valence π-electron densities at the heteroatom follow the
unexpected order As>N>P. This paper also considers core and valence
energy levels, valence ionization potentials, core ionizations,
correlation energies, and base strengths.

Phenylarsine reacts with aliphatic aldehydes to yield 2,4,6-
trialkyl-5-phenyl-1,3-dioxa-5-arsacyclohexanes [107]. The acid
catalyzed reaction proceeds in the manner shown below

$$C_6H_5AsH_2 + 3RC(O)H \xrightarrow{\text{HCl}} C_6H_5\text{---As} \underset{R}{\overset{R}{\diagdown}} \begin{array}{c} O \\ O \end{array} R + H_2O$$

R = CH₃, C₂H₅, C₃H₇
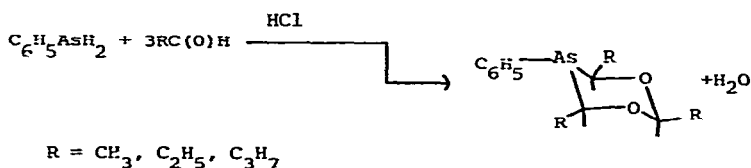
^{1}H NMR spectra indicate that compounds are made up of various isomers
differing with respect to the orientation of the substituent phenyl and/or
alkyl groups. The resonances of the annular protons indicated the
presence of at least four isomers of the trimethyl compound. The study
was initially undertaken for the purpose of preparing bis(α-hydroxyalkyl)phenyl
arsines, but all attempts to isolate α-hydroxyalkylarsines were unsuccessful.

In related investigations, Russian workers [108, 109] studied the reaction of phenylarsine with propenylisopropenylketone and isolated a new γ-ketoarsine, 1-phenyl-1,5-dimethyl-1-arsacyclohexanone-4. In its reaction with bis(β-methylvinyl) ketone and dibenzalacetone, phenylarsine does not enter into a cyclization reaction, but forms arsenobenzene and a monosubstitution product. The reaction of phenylarsine with methyl methacrylate gives low yields of the diester and its spirodilactone.

The preparation of spiroarsonium chlorides by the reaction between diphenylamine, di-p-tolylamine or N-phenyl-1-naphthylamine and arsenic trichloride has been attempted [110]. However, spiroarsonium chlorides could not be isolated. This is to be contrasted with the behavior of phosphorus chloride. In all cases, the heterocyclic chloroarsines were formed.

An NMR study on 1,3-dioxa(or thia)-2-arsacyclohexane has been carried out [111]. The derivatives studied were those shown below.
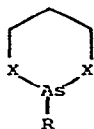
_9_	R = Cl, X = O		_12_	R = OMe, X = O
_10_	R = Br, X = O		_13_	R = C$_6$H$_5$, X = S
_11_	R = OMe, X = O			

The assignments of axial and equatorial protons were made from the observed characteristic values of J_{4a5a}. These values, together with those of J_{4e5e} indicate that these molecules exist almost entirely in one chair conformation which is to say, in an anancomeric equilibrium. The ring torsional angles were calculated from the vicinal coupling constants of the $CH_2CH_2CH_2$ grouping and values were ($\dot{r}$, compound, temp.), 59.7°, _9_, -43°, 60.3°, _10_, -70°, 59.7°, _11_, 34°, 60.4°, _12_, 34°, 65.7°, _13_, 34°. The analogous phosphorus compounds and 1,3-dioxanes are less puckered than the arsenic heterocycles. The degree of ring puckering is reflected in the values of the coupling constants.

Weustirk [112] and co-workers prepared some 10-arsaanthracenes.
These compounds were prepared in an effort to better understand why 10-phenyl-10-arsaanthracene is more stable than its parent compound or its 10-methyl and 10-ethyl derivative. The compounds prepared were 14, 15 and 16.

R

14 R = Cl
15 R = Br
16 R = OCH$_3$
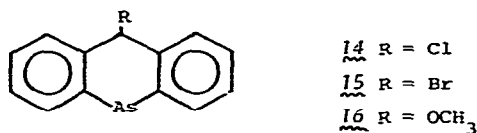
The synthetic procedure was that given below.

17   18a x=Cl   19a x=Cl
          18b x=Br   19b x=Br
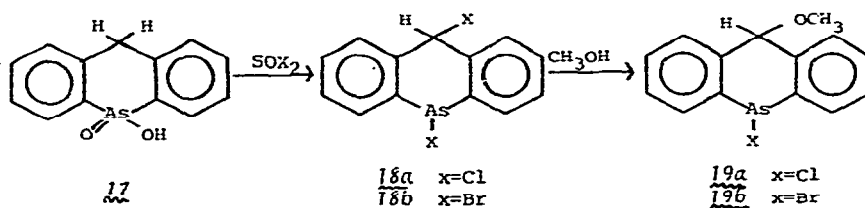
Treatment of 18a, 18b, 19a, or 19b with 1,5-diazabicyclo[5.4.0]undec-5-ene in THF in a high vacuum sealed vessel resulted in elimination of hydrogen halide and gave 14, 15 and 16 respectively. Ultraviolet measurements were made and it was concluded that the electronic effects of Cl, Br and OCH$_3$ do not lead to stabilization of the arsaanthracene system. The observed stabilization by a 10-phenyl substituent is concluded to be predominantly steric rather than electronic in nature. French investigators [113] prepared pentamethyl-2,3,7,8,10-pentamethyl-2,4,6,8,10- and pentamethyl-3,4,6,7,10-phenarsazine. Essentially, the synthetic procedure involved the action of methyl-magnesium iodide on the corresponding As-Cl bonded derivative. The study includes ^{1}H NMR and mass spectral data.

The reaction of NaAsHR with ClCH$_2$CH$_2$CH$_2$NH$_2$ yields the secondary 3-aminopropylarsines, RAs(H)CH$_2$CH$_2$NH$_2$ [114]. The latter react with aldehydes and ketones to form perhydro-1,3-azarsenines.
This paper describes the properties and reactivities of these heterocyclic compounds.

$$RAs(H)CH_2CH_2CH_2NH_2 + R'R''C = O \longrightarrow$$
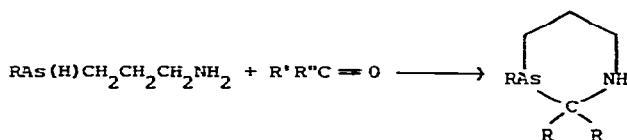
The cyclopolyarsines have been reviewed by Smith and Mills [115]. The coverage includes methods of preparation, physicochemical studies, chemical studies, chemical reations, and coordination compounds of cyclopolyarsines.

XII. Biochemical Aspects

Zingaro and Irgolic [116] have commented on the proposed mechanism for the biological methylation of arsenic. They point out that the conversion of methylarsonic acid to dimethylarsinic acid does not require a change in the oxidation number of arsenic with the accompanying electron transfer. Rather, a displacement of OH^- by CH_3^- may be involved with no change in the oxidation number (of arsenic).

High concentration of arsenic, 580 mg per kg. of ash, were reported in plants growing in the Alsar deposit of Macedonia, Yugoslavia [117]. Lakso and Peoples [118] measured the methylated arsenic and inorganic arsenic in the urine of cows and dogs fed sodium arsenate and potassium arsenite. The methylated arsenic concentration in cows and dogs fed arsenate peaked at 3.53 ppm and 6.23 ppm. respectively. Arsenite feeding caused these levels to peak at 4.78 ppm and 5.03 ppm. It was concluded that both As(III) and As(V) produce methylated arsenic. Because the dog is not a ruminant, it was concluded that the role site of arsenic methylation in cows is not in the rumen. The toxicity of 3-nitro-4-hydroxyphenylarsonic acid toward turkeys has been studied by Wise and co-workers [119] who reported it to be a growth depressant at all levels studied (down to 50 ppm). The effects of tryparsamide and mapharside on the fine structure of trypanosomes has been reported [120].

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