ARSENIC

ANNUAL SURVEY COVERING PAPERS ABSTRACTED IN VOLUMES 92-94 of *CHEMICAL ABSTRACTS* (1980-81)*

RALPH A. ZINGARO AND KURT J. IRGOLIC
Department of Chemistry, Texas A&M University,
College Station, Texas (U.S.A.)

Table of Contents

I. Introduction 67
II. Reviews and Books 68
III. Compounds Having a Metal-Arsenic Bond 68
VI. Compounds Having Arsenic-Nitrogen Bonds 71
V. Arsines and Polyarsines 73
VI. Compounds Containing Arsenic-Oxygen Bonds 75
VII. Compounds Containing Arsenic-Sulfur or Arsenic-Selenium Bonds 80
VIII. Compounds Containing Arsenic-Halogen (Halogenoid Bonds) 82
IX. Triorganyl Arsines 84
X. Arsonium Compounds and Arsenic Ylides 88
XI. Heterocycles Containing Arsenic as a Hetero Atom 93

I. *Introduction*

This review is concerned with the organic chemistry of arsenic and it covers the published literature in this field as abstracted in volumes 92, 93 and 94 of Chemical Abstracts. There exists a large body of literature which describes the synthesis and physical properties of coordination compounds in which organoarsines function as donor ligands. Because this body of literature is very extensive and, in fact, probably exceeds the coverage of this review, it is not included. As has been our policy in past years, it is assumed that this falls more properly in the literature which covers transition metal chemistry. Some new arsenic containing ligands as well as a few transition metal-arsenic compounds are included.

---

*Previous review see J. Organomet. Chem., 207 (1981) 121-184.

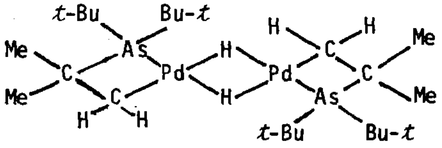
The authors again express their appreciation to the Robert A. Welch Foundation of Houston, Texas for their continued financial support which has helped considerably during the preparation of this review.

II. *Reviews and Books*

If any books devoted to the subject of organoarsenic compounds have been published during the period covered by this review, they have not come to our attention. A brief review which describes methods for the synthesis of arsines has been prepared by Russian authors (1). Wardell (2) continues to furnish invaluable information to the organoarsenic chemist in his periodic review of Group V chemistry. Complex ions involving coordination of metal ions to alkylarsonic acids and dialkylarsinic acids are the subject of a review by Shimura (3).

III. *Compounds Having a Metal-Arsenic Bond*

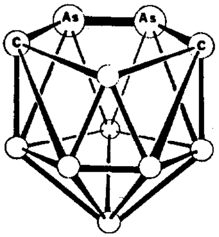
Goel and Ogini (4) have investigated the reaction between *tris* (*t*-butyl) arsine and Na_2PdCl_4 in absolute ethanol. This affords the air-stable hydride, $PdHCl[As(t\text{-}Bu)_3]_2$. In this reaction a Pd-Cl bond is converted into a Pd-H bond. This compound has a *trans* structure (^1H NMR spectrum). This hydride undergoes a slow intramolecular condensation at room temperature in benzene to give the metalated hydrido-bridged dinuclear Pd(II) complex. The structure of the *trans* form, as reported by the investigatiors, is shown below.



Malisch (5), et al., have studied the reaction between dimethylchloroarsine and $[C_5H_5(CO)_3M]Na$ or $C_5H_5(CO)_3M\text{-}Si(CH_3)_3$, where M = Cr, Mo, W.

This reaction yields dimethylarsanes of the formula, $C_5H_5(CO)_3M\text{-}As(CH_3)_2$(I). The latter undergo thermal decomposition in toluene with loss of CO to give M-As-M, arsenic-bridged species of the type $[C_5H_5(CO)_2M\text{-}As(CH_3)_2]_2$, M = Mo, W. Under photolytic conditions the additional products, *trans*-$C_5H_5(CO)_2[C_5H_5(CO)_3M\text{-}As(CH_3)_2]M\text{-}(AsCH_3)_2$ and [*trans*-$C_5H_5(CO)_2M\text{-}As(CH_3)_2]_x$ are formed. Reaction of I with alkyl halides or Me_3SiI results in the formation of the cationic complexes $[C_5H_5(CO)_3M\text{-}As(CH_3)_2R]X$ where R = CH_3, $CH_2C(O)C_6H_5$, $CH_2Si(CH_3)_3$, $Si(CH_3)_3$; X = Br, I. With Cl_2 or Br_2 the extremely labile diahalogen adducts, $C_5H_5(CO)_3M\text{-}As(CH_3)_2X_2$ are formed. The transition metal-arsenic bond is cleaved by HCl, CF_3CO_2H, $(CH_3)_3SnH$, Na/Hg, CH_3MgI and $(CH_3)_3PCH_2$ under very mild conditions.

The synthesis of heteroatom boranes containing two arsenic atoms has been reported (6). The reaction between $B_{10}H_{14}$ and Na_2SeO_3 gives the anion, $B_{10}H_{11}Se^-$. This anion reacts with As_2O_3 in basic solution to form, in low yield, yellow $B_8H_8As_2Se$. The positions of the heteroatoms in the molecules is not established. $B_8H_8As_2S$ in KOH treated with $Et_3N/C_5H_6/CoCl_2$ produces red $B_7H_7As_2SCo(C_5H_5)$. The reaction of the carborane, $B_7C_2H_{13}$ with AsI_3 and Et_3N forms $B_7C_2H_9As_2$. The ^{11}B NMR spectrum is characterized by five doublets with relative areas 1:2:2:1:1 and this suggests the presence of a mirror plane. Together with ^1H NMR data, the following structure is proposed.



Proposed structure of $B_7C_2H_9As_2$

The photolysis of $(C_5H_5)Co(CO)_2$ and $B_7C_2H_9As_2$ in THF gives low yields of $(C_5H_5)Co(B_7C_2H_9As_2)$.

The vibrational analysis of As-B adducts is the subject of the doctoral dissertation of Khasrou (7). Among the molecules studied are Me_3AsBX_3 and the deuterated analogues. Both i.r. and Raman spectra as well as force constant calculations are presented. Changes in $\nu(M - C)$ and $\nu(M - H)$ force constants show progressive decreases with increasing methyl substitution.

Becker and co-workers (8) have reported on silylarsanes. They prepared what is formulated as, but without unequivocal identification, "Na_3As/K_3As" by the reaction between Na/K alloy and arsenic powder. The alkali metal arsenide undergoes reaction with chlorotrimethylsilane in dimethyoxyethane to form *tris*(trimethylsilyl)arsane, $(Me_3Si)_3As$(I). The reaction between I and MeLi gives lithium*bis*(trimethylsilyl)arsenide, $[(CH_3)_3Si]_2AsLi$ (II). II crystallizes with two molecules of THF on one molecule of dimethoxyethane. Some of the reactions of II are shown belown.

$$[(CH_3)_3Si]_2AsLi + RX \rightarrow R\text{-}As[Si(CH_3)_3]_2$$

$$R = CH_3\ ,\ C_2H_5\ ,\ (CH_3)_2CH\ ,$$

$$C_6H_5CH_2\ ,\ (C_6H_5)_2CH$$

$$2[(CH_3)_3Si]_2AsLi + CH_2Cl_2 \rightarrow H_2C(As[-Si(CH_3)_3]_2)_2$$

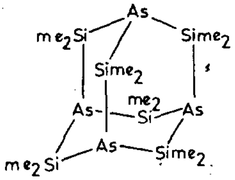
$$[(CH_3)_3Si]_2AsLi + (C_6H_5)_2\,CHCl \rightarrow$$

$$[(CH_3)_3Si]_2As\,Cl + (C_6H_5)_2CHLi$$

$$[(CH_3)_3Si]_2AsCl + [(CH_3)_3Si]_2AsLi \rightarrow$$

$$[(CH_3)_3Si]_2As\text{-}As[Si(CH_3)_3]_2$$

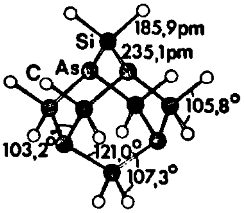
Dichlorodimethylsilane undergoes reaction with II to yield *bis*[*bis*(trimethylsilyl)arsano]dimethylsilane, $(CH_3)_2Si(As[Si(CH_3)_3]_2)_2$(III). When III is heated it forms I and dodecamethyl-hexasila-tetraarsa-adamantane (below).



Silyldiazoalkanes containing arsenic have been synthesized by Glozbach and Lorberth (9). The reaction of Me_3SiCHN_2 with Me_2AsNMe_2 using Me_3SnCl as a catalyst give $Me_3Si(Me_2As)CN_2$. The As-C fundamental stretching frequency is reported at 520 cm^{-1} and the asymmetric component at 545 cm^{-1}.

The corresponding symmetric and asymmetric stretches are reported at 545 and 575 cm^{-1} for $(Me_2As)_2CN_2$.

The crystal structure of dodecamethyl-hexasila-tetraarsa-adamantane $(Me_2Si)_6As_4$ has been determined (10). The structure is shown below.



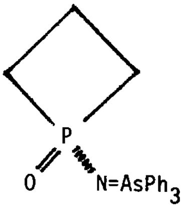
The bond angles at the arsenic atoms are 103.2° and the As-Si bond distance is 235.1 pm.

IV. *Compounds Having Arsenic-Nitrogen Bonds*

The reaction between diethylamino-chlorophenylarsine and thiols in benzene at 50° gives thioesters of dialkylamidophenylarsonous acid (11).

$$PhClAsNEt_2 + HSR \rightarrow Ph(RS)AsNEt_2$$

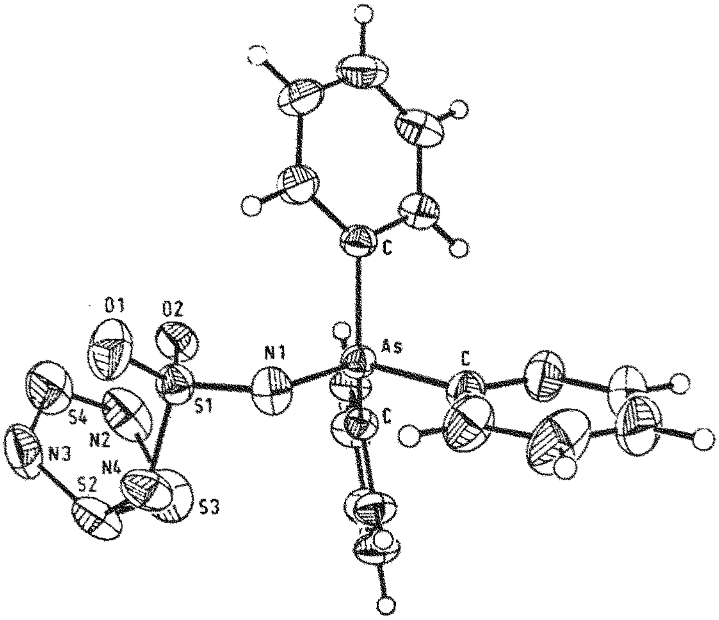
The reaction of $PhAs(NEt_2)_2$ with RSH gives $Ph(RS)AsNEt_2$. The reaction of LiR, R = $HC(SiMe_3)_2$ or $N(SiMe_3)_2$ $AsCl_3$, depending of the stoichiometric ratios, affords a new class of compounds (12). These are $Cl_2As[CH(SiMe_3)_2]$ or $ClAs[CH(SiMe_3)_2]_2$. Reduction of the monochloride in toluene by photolysis with the olefin $[\mathrm{Et\overline{N(CH_2)_2NEtC}} = \mathrm{\overline{CN(Et)(CH_2)_2N}Et}]$ gives the persistent free radicals species, $\cdot As[CH(SiMe_3)_2]$. The electron spin resonance characteristic of this species is reported. Crystalline *N*-phosphinoyl-arsoranyl-ideneamine (below) has been reported by Harger and Stephen (13)



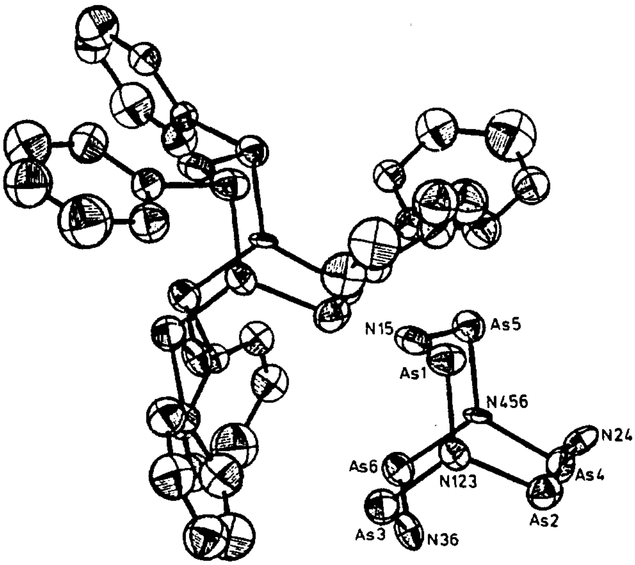
Three synthetic methods are described. The first involves the reaction between *r*-1-(*N*,*N*-dichloroamino)-2,2-*t*-3,4,4-pentamethyl-phosphetan 1-oxide and triphenylarsine in methylene chloride. The second method involves the reaction between triphenylarsine and *r*-1-amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide with diacetoxy-triphenylarsorane.

Arsenic compounds which possess an adamantane like skeleton are the subject of a survey by Kober (14).

Roesky and co-workers (15) have investigated the (8→5) ring contraction of the eight-membered ring compound, $S_4N_4O_2$, when it is allowed to react with Ph$_3$As. The crystal structure of the compound formed, triphenylarsorandiylaminosulfonylimino-1λ^4,2,4λ^4,3,5--trithiadiazol has the crystal structure shown below.



The crystal structure of 2,4,6,8,9,11-hexapheny-bicyclo-[3,3,3,]-2,4,6,8,9, 11-hexaarsa-1,3,5,7,10-pentaaza-undecane benzene has been determined (16) and is shown below.

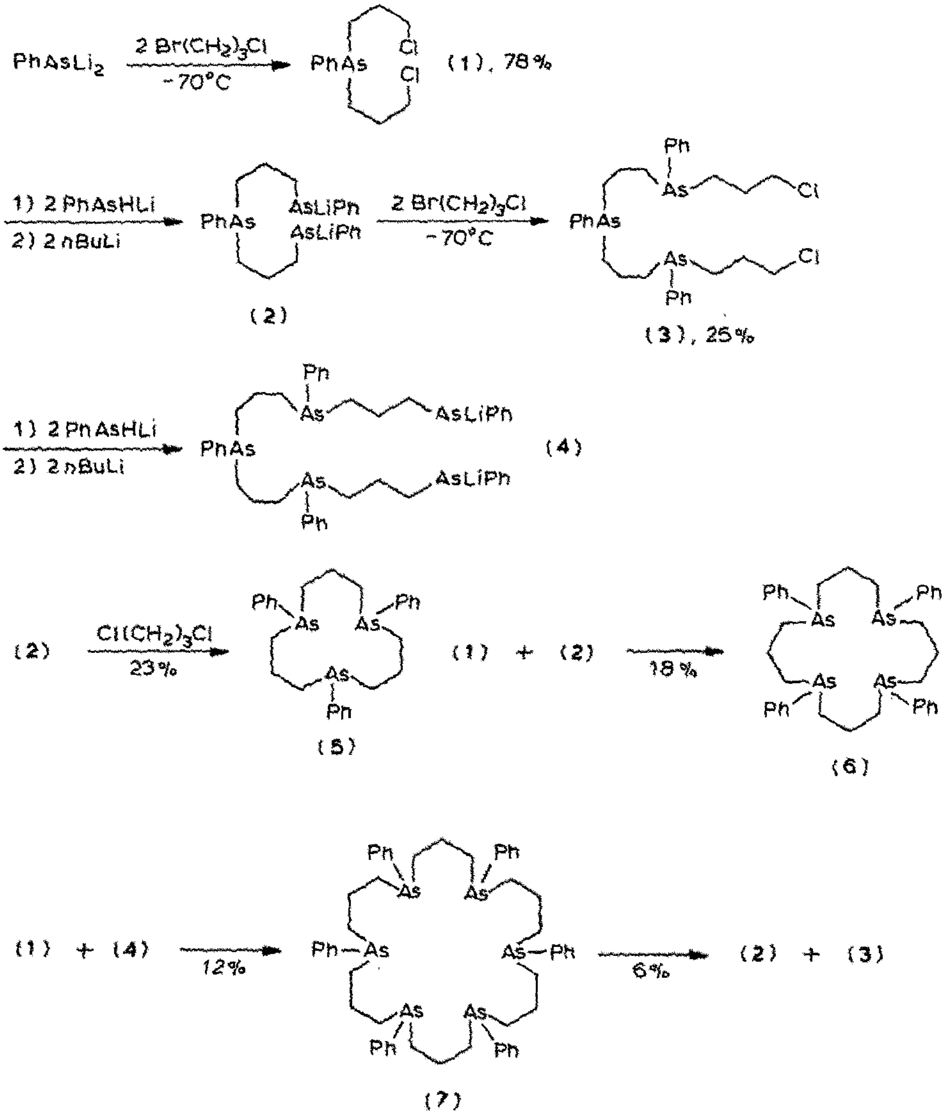


V. *Arsines and Polyarsines*

Many polyarsines have been synthesized in conjunction with the study of the coordination chemistry of transition metals. A ligand containing both boron and arsenic has been reported by Fussstetter, et al. (17). The reaction is described by the following equation.

$$Me_2B\text{-}NMeLi + ClAsMe_2 \rightarrow Me_2B\text{-}NMeAsMe_2 + LiCl$$

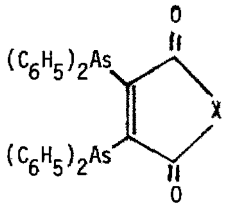
The bidentate ligand, 2, 11-*bis*(diphenylarsinomethyl)benzo[c]-phenanthrene has been prepared by the reaction between $LiAs(C_6H_5)_2$ and 2,11-*bis*(bromomethyl)-benzo[c]-phenanthrene (18). Crown arsines which function as multielectron ligands for transition metals have been synthesized by Ennen and Kauffmann (19). The sequence of reactions and the molecules synthesized are outlined in the following scheme.


PhAsLi$_2$
2 Br(CH$_2$)$_3$Cl
-70°C
PhAs
Cl
Cl
(1), 78%
1) 2 PhAsHLi
2) 2 nBuLi
AsLiPh
AsLiPh
(2)
2 Br(CH$_2$)$_3$Cl
-70°C
Ph
As
Cl
(3), 25%
(4)
Cl(CH$_2$)$_3$Cl
23%
(5)
(1) + (2)
18%
(6)
(1) + (4)
12%
(7)
6%
(2) + (3)

The synthesis of the hexadentate ligand, P,P,P',P'-*tetrakis*(2-diphenylarsinoethyl) -α,α'-diphospha-*p*-xylene has been reported (20). Tetraethyl-α,α' -*p*-xylene diphosphonate in dry ether was treated with $LiAlH_4$ and the resultant phosphine was allowed to react with diphenylvinylarsine and potassium-*t*-butoxide. The addition of dialkylarsines to acetylenes gives arsines containing an olefinic substituent (21).

$$R\text{-}C{\equiv}CH + R'_2\,AsH \rightarrow R\text{-}CH{=}CHAsR'_2 + R(R'_2As)C{=}CH_2.$$

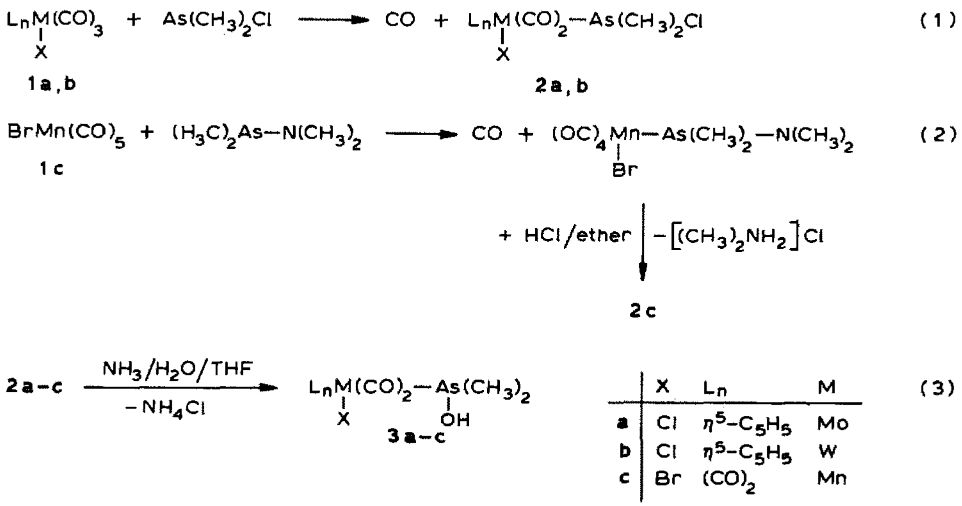
A series of arsines of the type R'_2AsH, where R is C_3- C_6-alkyl were prepared by the reaction of the arsenous acid anhydride with the Grignard reagent followed by hydrogen reduction (22). Methylene*bis*(diarylarsines) have been synthesized by the reactions of the appropriate Grignard reagent in THF with methylene*bis*(dichloroarsine) (23). The resultant arsines are readily oxidized to the arsine oxides or add sulfur to form the arsine sulfides. The reaction between trimethylsilyldiphenylarsine, $Me_3SiAs(C_6H_5)_2$ and the anhydride of dichloromaleic acid gives arsines of the type shown below (24).



X = O,S

VI. *Compounds Containing Arsenic-Oxygen Bonds*

Arsinous acids, R_2AsOH, are intrinsically unstable. Lindner and Gumz (25) have synthesized stable compounds containing $(CH_3)_2AsOH$ coordinated to a metal. The types of compounds prepared and the method of preparation is given by the following scheme.



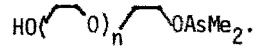
$$\underset{\mathbf{1a,b}}{\underset{X}{L_nM}(CO)_3} + As(CH_3)_2Cl \longrightarrow CO + \underset{\mathbf{2a,b}}{\underset{X}{L_nM}(CO)_2{-}As(CH_3)_2Cl} \qquad (1)$$

$$\underset{\mathbf{1c}}{BrMn(CO)_5} + (H_3C)_2As{-}N(CH_3)_2 \longrightarrow CO + (OC)_4\underset{Br}{Mn}{-}As(CH_3)_2{-}N(CH_3)_2 \qquad (2)$$

$$\xrightarrow[\;]{+\ HCl/ether \ \ -[(CH_3)_2NH_2]Cl} \mathbf{2c}$$

$$\mathbf{2a{-}c} \xrightarrow[-NH_4Cl]{NH_3/H_2O/THF} \underset{\mathbf{3a{-}c}}{\underset{X}{L_nM}(CO)_2{-}\underset{OH}{As}(CH_3)_2} \qquad (3)$$

	X	Ln	M
a	Cl	η^5-C_5H_5	Mo
b	Cl	η^5-C_5H_5	W
c	Br	$(CO)_2$	Mn

Phung, Chi and Kober (26) have studied the reaction between $Me_2As\text{-}NMe_2$ and tri- or tetraethylene glycol which results in the formation of cacodyl derivatives . The latter react with aminoarsines to yield "pode"-type molecules. Some typical reactions are shown below.

$$Me_2AsNMe_2 + HO\text{-}CH_2CH_2OCH_2CH_2OCH_2CH_2OH \rightarrow$$

$$Me_2As\,OCH_2CH_2OCH_2CH_2OCH_2CH_2OH \quad (I)$$

$$As(NMe_2)_3 + 3(I) \rightarrow As[\text{-}OCH_2CH_2OCH_2CH_2OCH_2CH_2AsMe_2]_3$$

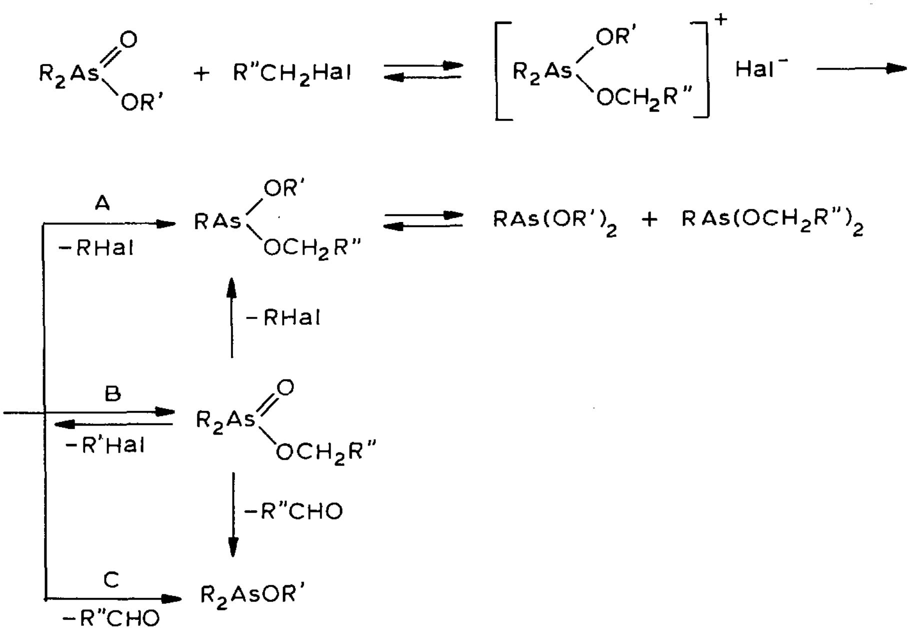
$$As(NMe_2)_3 + 3\ HOCH_2CH_2OCH_2CH_2OCH_2CH_2Cl \rightarrow$$

$$As[\text{-}OCH_2CH_2OCH_2CH_2OCH_2CH_2Cl]_3$$

A number of similar derivatives of tri- and tetraethylene glycol were synthesized and characterized. They are a group of liquids having high boiling points.

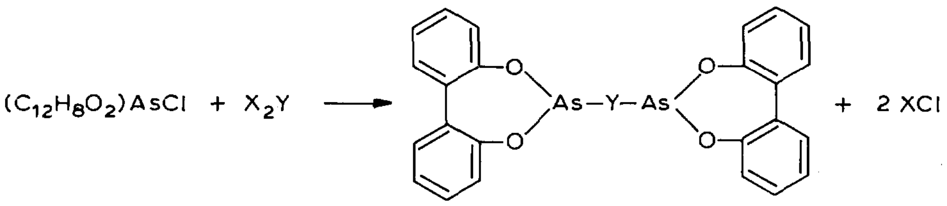
The products formed by the oxidation of di-*m*-tolylarsines with potassium permanganate have been identified (27). Thus, oxidation of $(m\text{-}MeC_6H_4)_2AsR$ gives $(m\text{-}HO_2CC_6H_4)_2As(O)R$. $(m\text{-}MeC_6H_4)_2AsCl$ gives by reaction with NaOH, $[(m\text{-}MeC_6H_4)_2As]_2O$. The latter, following oxidation by $KMnO_4$ gives $(m\text{-}HO_2CC_6H_4)_2As]_2O$. The ultra-violet spectra of a series of ring-substituted arylarsonic acids have been investigated (28). A linear correlation of K-band shifts with the parameters of Doub and Vandenbelt was obtained. The vibrational spectra of 15 benzenearsonic acids have been investigated by IR and Raman spectroscopy (29).

The reactions of diphenyl- and dialkylarsinic esters as well as dipropyl phenylarsonate with alkyl halides has been studied by Gamayurova, et al. (30). The reaction follows three main courses: retro-Arbuzov rearrangement, exchange reaction, and oxidation reduction. The proposed scheme is shown below.



R = Alk, Ar, OAlk; R' = Alk; R" = Alk, Ar

Andrae and Gebel have reported on the reactions of 2,2'-diphenylenedioxyarsenic(III) chloride. With liquid ammonia, aniline, and diethylamine the corresponding amine derivatives are formed. The chlorine is replaced by C_6H_5- when the title compound reacts with C_6H_5MgBr in tetrahydrofuran. The reaction with silver oxide and with silver sulfide or hydrogen sulfide proceeds as follows (31).



X = Ag; Y = O
X = Ag, H; Y = S

With phenol, in the presence of triethylamine, chlorine is replaced by $C_6H_5O^-$. In toluene, the -As-Cl bond, reacts with sodium to produce the -As-Na derivative which reacts with the title compound to yield the -As-As-derivative.

Methyl and trifluoromethyl arsines undergo oxidative addition reactions with *bis*(trifluoromethyl)nitroxyl, $(CF_3)_2NO$ to yield pentavalent derivatives of arsenic (32). The authors propose the following stepwise radical addition:

$$(CF_3)_2CH_3As \; + \; (CF_3)_2NO \; \rightarrow \; (CF_3)_2CH_3AsON(CF_3)_2$$

$$(CF_3)_2CH_3AsON(CF_3)_2 \; + (CF_3)_2NO \; \rightarrow \; (CF_3)_2CH_3As[ON(CF_3)_2]_2$$

The compounds are extremely moisture sensitive and yield *bis*(trifluoromethyl) hydroxylamine on hydrolysis. The reaction with anhydrous HCl proceeds as follows:

$$CH_3(CF_3)_2As[ON(CF_3)_2]_2 \; + HCl \; \rightarrow \; CH_3(CF_3)_2AsCl_2 \; + (CF_3)_2NOH$$

A ^{13}C NMR study of arsenic(III) dihydroxydicarboxylate complexes has been reported (33). Sodium salts of the anionic complexes of tartrate^{4-} and its methyl substituted derivatives with arsenic(III) were prepared and the sterochemistry in aqueous solutions studied by ^{13}C NMR spectroscopy. The compounds containing (±)-tartrate^{4-}, *threo*-monomethyltartrate^{4-}, and (±)-dimethyltartrate^{4-} are binuclear in solution with *dd* and *ll* forms more stable than *dl*. Solid salts of arsenic(III) with *ms*-dimethyltartrate^{4-} and with *erythro*-monomethyltartrate^{4-} were also prepared.

Tris(isopropyl) arsenate was prepared by the esterification of H_3AsO_4 with isopropanol (34). Its infra-red and Raman spectra were recorded, the dipole moment, $\mu = 2.49D$ was measured and the dielectric constant and the indices of refraction in CCl_4 were also determined. The values reported are: $\alpha = 17.450$, $\gamma = -1.289$, $P_o = 178.007\ cm^3$. In solution and in the liquid state the compound exists as an equilibrium mixture of two conformers with symmetries close to C_3 and C_5. Both conformers were prepared and characterized in the cyrstalline state.

Edwards and co-workers have reported on the hydrolysis of arsenate esters (35,36). As-O bonds are cleaved 10^5-10^6 times more rapidly than P-O bonds. Arsenate(V) esters are known to be very sensitive to hydrolysis while the analagous phosphate esters are quite inert. Arsenate esters are also very labile with respect to hydrogen exchange. The latter property makes study of the rate of exchange possible by means of dynamic nuclear magnetic resonance spectroscopy. Studies of the rate of alcohol exchange with trialkyl arsenates showed the absence of any kinetic isotope effect and suggests transfer of a proton after the rate-determining formation of a 5-coordinate intermediate.

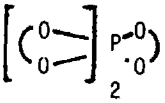
$$OAs(OR)_3 + R'OH \rightleftarrows OAs(OR)_3(OHR')$$
$$OAs(OR)_2(OR')+ROH \rightleftarrows OAs(OR)_2(OR')(HOR)$$

The mechanism requires a rapid proton transfer between alkoxyl groups of the trigonal-bipyramidal intermediate.

The rates of hydrolysis of a series of arsenate esters, $OAs(OR)_3$, R=Me, Et, *n*-pentyl, or isopropyl were measured in methanol or ethanol at low water concentrations. The hydrolysis of $(MeO)_3AsO$ in methanol is first order in ester and water. Hydrolysis rates of the esters decreased in the order methyl> ethyl> *n*-pentyl > isopropyl. The experimental data were found to be consistent with an associative mechanism involving the proposed formation of a five-coordinated arsenic intermediate, $OAs(OR)_3(H_2O)$.

A polarographic investigation of the reactions between As(III), tartaric acid (H_2T) and DCTA, 1,2-diaminocyclohexane, N,N,N',N'-tetraacetic acid has been carried out by Elenkova and Tsoneva (37). Conditional stability constants were calculated for As(III) complexes at given pH values and variable ligand concentrations from changes in the limiting currents. It was found that DCTA (H_4L) formed a complex having a stoichiometry given by $[As(OH)_2HL]^{2-}$ and the complex formed between As(III) and H_2T was $[As(OH)_2T]^-$.

Kabachnik (38) has carried out a detailed ESR study of phosphorus-containing radicals of the type



where O⌒O stands for a phenylene-dioxy group. The radical has an octahedral symmetry and the unpaired electron "wanders" over six oxygen atoms. This is termed by Kabachnik as "wandering valency." This phenomenon has also been observed in analogous arsenic compounds.

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

S-dialkylarsino derivatives of 2-deoxy-1- and 6-thio-D-*arabino*-hexose have been synthesized by Rosenthal and Zingaro (39). 1-*S*-dialkylarsino derivatives of 3,4,6-tri-*O*-benzoyl-2-deoxy-1-thio-β-D-*arabino*-hexaopyranose, where the alkyl group is methyl, *n*-propyl and *n*-butyl were prepared. The reaction took place between the appropriate thio sugar and dialkylhalo-arsine in methylene chloride in the presence of pyridine at pH 7.

Compounds having As-S, As-Se and As-Te bonds of the general formula $R_2As\text{-}XR'$, where X = S, Se, Te and R' = CH_3, CF_3, were synthesized by Dehnert and co-workers (40). Characteristic methods of preparation are shown below. Gatilov and Perov (41) have investigated the reaction

$$Me_2AsCl + MeXH \xrightarrow{Me_3N} Me_2AsXMe$$

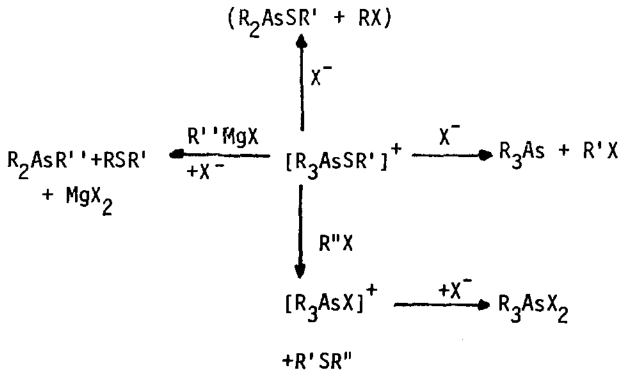
$$Me_4As_2 + Me_2X_2 \longrightarrow 2\ MeAsXMe$$

$$X = S, Se, Te$$

$$2(CF_3)_2AsI + (CF_3Se)_2Hg \longrightarrow 2(CF_3)_2AsSeCF_3$$

$$Me_4As_2 + (CF_3)_2Se_2 \longrightarrow 2\ Me_2AsSeCF_3$$

between triethyl(ethylthio) arsonium bromide and electrophiles, such as HBr, in order to better understand the reaction between tertiary arsine sulfides and alkyl halides. The first step in the reaction between R_3AsS with alkyl halides involves the formulation of an arsonium (quasiarsonium) salt whose stability depends upon the electronegativities of the substituent groups. The reactions of the arsonium salt are outlined as follows



If R and R' are electron donor groups, the salt is quite stable irrespective of the nucleophilicity of the anion. The presence of even one electron-acceptor (aryl) groups in $[R_3AsSR']$ leads to destabilization. Weak nucleophiles such as BF_4^- and RX, R=alkyl, are unreactive foward the cation.

Tertiary arsine sulfides react with acyl halides through quasiarsonium salt formation (42).

$$Et_3AsS + CH_3COCl \rightarrow \underset{\underline{A}}{[Et_3AsSCOCH_3]^+Cl^-}$$

$$\begin{tikzcd}
 & Et_2AsSCOCH_3 \\
\underline{A} \arrow[ur] \arrow[r, "+CH_3COCl"] & (C_2H_5)_3AsCl_2 + (CH_3CO)_2S \arrow[d] \\
 & (C_2H_5)_2AsCl + C_2H_5Cl
\end{tikzcd}$$

$$2\ Et_3AsS \rightarrow Et_4As^+\ S_2AsEt_2^- \quad (\underline{B})$$

$$\underline{B} \xrightarrow{\Delta} 2Et_2AsSEt$$

The reactions between the reagents was studied thermogravimetrically and by differential thermal analysis. A paper entitled "Reaction of tertiary arsine sulfides with organomagnesium compounds" has been published (43) by the same authors.

1,2-*Bis*(diphenylarsinothioyl)ethane forms a weak inclusion compound with benzene, but toluene, *p*-xylene and cyclohexane do not form adducts with this host (44).

Ligands of the type R_2AsXR', where X=S, Se or Te and R'= Me or CF_3 react according to the following reaction (45)

$$Cr(CO)_5(THF) + R_2AsXR' \rightarrow Cr(CO)_5AsR_2XR' + THF$$

These compounds were studied by infra-red and ^1H and ^{19}F NMR spectroscopy.

Arsine sulfides and selenides were prepared by the oxidative addition of sulfur or selenium to the corresponding trivalent arsines (46). Some of the arsine sulfides (selenides) are shown below.

$N[CH_2CH_2As(X)Me_2]_3$ $H_3C(CH_2Cl)C[CH_2As(X)Me_2]_2$

$(ClCH_2)_2C[CH_2As(X)Me_2]_2$

$X = S,Se$

These molecules coordinate, through sulfur, or selenium, to Co(II) and Ni(II).

Cyclopentadienyl (Cp) molybdenum or tungsten carbonyls bonded to dimethylarsine sulfide react with acetyl halides (47). The first step in this reaction involves the formation of the salt, $[Cp(CO)_2PMe_3M\text{-}AsMe_2SC(O)Me]^+X^-$, where M = Mo, W; X = Br,Cl. The addition of a second mole of MeC(O)X brings about conversion into the salts of the type $[Cp(CO)_2PMe_3M\text{-}AsMe_2X]^+X^-$ with the elimination of $(Me_2CO)_2S$. Structures of the ionic dihalogen adducts is inferred from infra-red, NMR and conductivity data.

The crystal structure of $(C_6H_5As)_4$ has been determined (48). The molecule is made up of staggered eight-membered As-S rings. In the crystal, the arsenic-sulfur rings are "stacked like coins." The As-S bond distances are 2.262(8) and 2.25 Å. The As-S-As' bond angle is 96.58° and and the S-As-S bond angle is 102.07°. The As-C bond distance is 1.99(4) Å. Also determined by X-ray crystallography were the crystal structures of triethylarsine sulfide and triphenylarsine sulfide. In the triethyl compound the symmetry is C_{3v} and the As-S bond distance is 2.115 Å (49)

V111. *Compounds Containing Arsenic-Halogen (Halogenoid) Bonds*

Dephenylchloroarsine is chlorinated by selenium tetrachloride or tellurium tetrachloride to diphenylarsenic trichloride (50). The trichloride is readily hydrolyzed to diphenylarsinic acid. In this reaction the tetrachlorides of selenium or tellurium are reduced to the free elements.

The reactions between arsenic(III) halides and metal halides have been studied. Triarylarsines undergo oxidative addition reactions with copper(II) or mercury(II) halides. The metals are reduced to the monovalent state and the arsenic compounds are oxidized to the pentavalent state. The reactions, carried out in dry acetone, are summarized as follows.

$$\mathrm{Ar_3As + 2MX_2 \rightarrow Ar_3AsX_2 + M_2X_2}$$

$$\mathrm{M = Cu(II),\ Hg(II)}$$

$$\mathrm{Ar = phenyl,}\ p\text{-}\mathrm{tolyl}$$

Dialkylarsinous chlorides undergo halogen exchange with potassium thiocyanate or potassium cyanide in acetone.

$$\mathrm{R_2AsCl + KCN \rightarrow R_2AsCN + KCl}$$

$$\mathrm{R_2AsCl + KSCN \rightarrow R_2AsSCN \rightarrow R_2AsNCS}$$

The As-CN bond undergoes alkaline hydrolysis to the anhydride of the arsinous acid (52).

$$\mathrm{2\ Ar_2AsCN \xrightarrow{OH^-} (Ar_2As)_2O + NH_3 + CO_3^{2-}}$$

$$\mathrm{Ar} = p\mathrm{EtC_6H_4}$$

Arsenic trichloride and triphenylarsine oxide react exothermally, in the absence of any solvent to yield triphenylarsenic dichloride (53). When alkyl*bis*(*p*-tolyl) arsine dichlorides, are hydrolyzed by water to the hydroxyarsonium chlorides, $[\mathrm{RAr_2As(OH)}]^+\ \mathrm{Cl}^-$. However, in sodium hydroxide solution, the alkyl*bis*(*p*-tolyl)arsine oxides, $\mathrm{RAr_2AsO}$ are formed (54).

Some reactions of aromatic-$\mathrm{AsF_6}$ molecules have been reported (55). $\mathrm{O_2AsF_6}$ reacts with pentafluoropyridine and octafluorotoluene to give $\mathrm{C_5F_5NAsF_6}$ and $\mathrm{CF_3C_6F_5AsF_6}$. Pyrolysis of $\mathrm{C_6F_6AsF_6}$, $\mathrm{C_5F_5NAsF_6}$ and $\mathrm{CF_3C_6F_5AsF_6}$ yields an equimolar mixture of the parent fluorocarbon and an isomer-specific cyclohexadiene. Hydrolysis of $\mathrm{C_{10}F_8AsF_6}$ yields an equimolecular mixture of $\mathrm{C_{10}F_8}$ and an isomer-specific quinone, $\mathrm{C_{10}F_6O_2}$. $\mathrm{AsF_5}$ and benzene react to give $\mathrm{(C_6H_5)_2AsF_2{}^+AsF_6{}^-}$. The latter reacts quantitatively with CsF to give $\mathrm{(C_6H_5)_2AsF_3}$ and $\mathrm{CsAsF_6}$. Based on ^{19}F NMR studies it is concluded that $\mathrm{(C_6H_5)_2AsF_3}$ is a rigid trigonal bipyramid with the phenyl groups occupying equatorial positions. The reaction of benzene with $\mathrm{O_2AsF_6}$ or $\mathrm{C_6F_6AsF_6}$ yields a mixture of $\mathrm{(C_6H_5)_2AsF_2{}^+AsF_6{}^-}$ and the polyphenylene salt, $\mathrm{(C_6H_4)_xAsF_6}$, $1.8<x<4.4$. The polyphenylene salt has only moderate electrical conductivity which indicates that it is a delocalized electron solid. In a related study, the reaction product of pyrene and arsenic pentafluoride has been characterized by ^{19}F NMR measurements (56). The results are interpreted in terms of a simple structural model. A very strong electron exchange is attributed to a strong overlap of the pi orbitals on neighboring aromatic radical ions. A structural model is proposed in which the pyrene species are stacked with the fluoride species residing outside of the columns formed by pyrene stacking. The arsenic fluoride species probably include AsF_6^-, AsF_5 and AsF_3. The fluorine-arsenic species rotate with AsF_6^- and AsF_5 forming a fluxional dimer. At 200°K the rotational motion diminishes and the AsF_6^- ions combine with one or more AsF_5 molecules to formed monovalent charged dimers or oligomers. The oligomers rotate about their four-fold axis. The model is consistent with the known stability of $As_2F_{11}^-$ at low temperatures.

Barlos, et al, (57) have measured ^{35}Cl NMR chemical shifts in $AsCl_3$, H_3CAsCl_2 and $(H_3C)_2AsCl$.

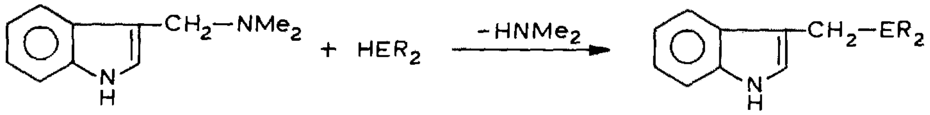
IX. *Triorganyl Arsines*

Arsines in which one of the substituents is an arylsulfonamido group have been reported (58). The procedure used involved the addition of the disubstituted arsine to the *N*-arylsulfonylbenzaldimine at ambient temperature.

$$RC_6H_4SO_2N{=}CHPh + HAsR'_2 \rightarrow RC_6H_4SO_2NHCH(Ph)AsR'_2$$

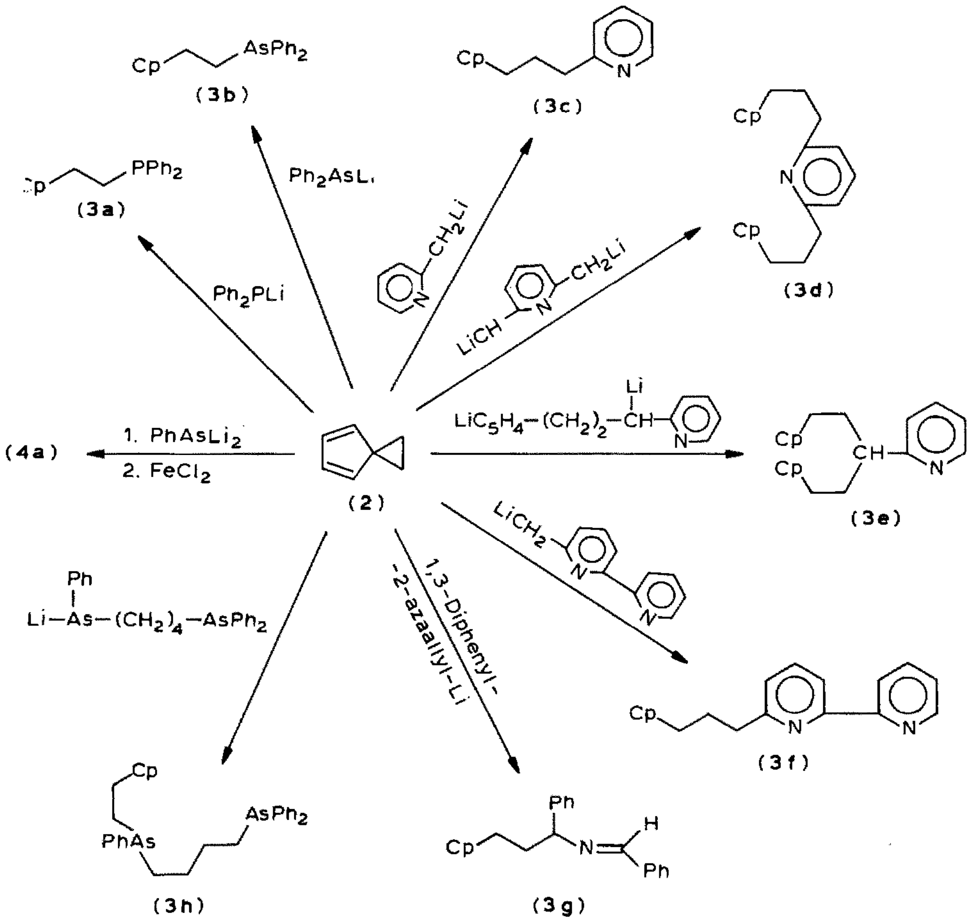
$$R{=}H,\ Me;\ R'{=}Ph$$

2-Hydroxybenzylamines or 2- and 4-aminobenzylamines react with diphenylarsine at 140-150°C to yield substituted benzylarsines (59). An elimination-addition mechanism or a substitution-mechanism are proposed. 3-Dimethylaminomethyl indole reacts with secondary arsines according to the proposed mechanism to give indolylmethyl arsines. The types of molecules synthesized are shown below.

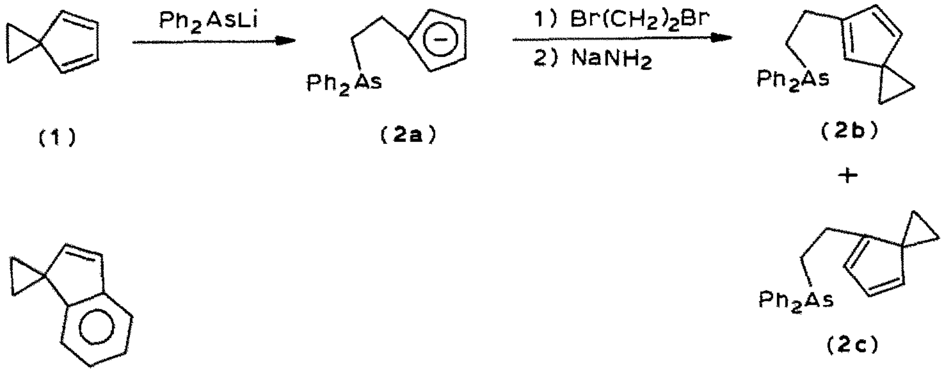


E	P	As	As
R	Ph	Ph	Cy

A Russian patent (60) describes the synthesis of mono or diacetylenic arsines, QC≡CAsRPh, where Q is a thia- or oxacyclohexa-2,3-ene. In some cases Q has an acetylenic group in the 4- position bonded to arsenic. The method of preparation involved the reaction of QAlLi or QC≡CAlLi with the haloarsine in THF or pyridine at 50-100°C followed by hydrolysis with HCl. Some reactions between *spiro*hydrocarbons and lithium arsines have been reported. These yield a variety of arsines (61).


(3a)
(3b)
(3c)
(3d)
(3e)
(3f)
(3g)
(3h)
(4a)
(2)
Ph₂PLi
Ph₂AsLi
1. PhAsLi₂
2. FeCl₂
LiC₅H₄—(CH₂)₂—CH(Li)—
1,3-Diphenyl-2-azaallyl-Li
Ph
Li—As—(CH₂)₄—AsPh₂
Cp
AsPh₂
PPh₂
PhAs
N
CH
H
Ph
CH₂Li
LiCH
LiCH₂

Similar reactions investigated at the same laboratory have yielded additional arsines (62).



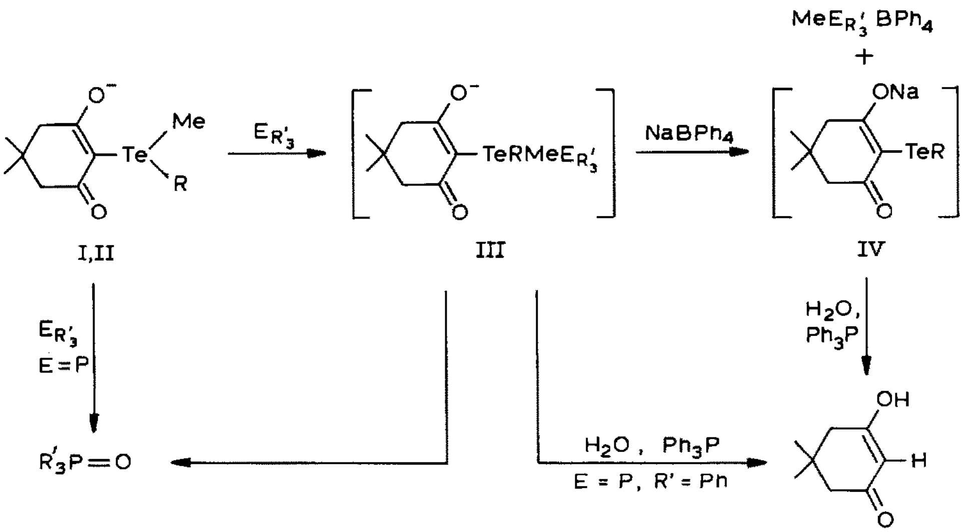
(1) (2a) (2b) + (2c)

(3)

The basicity of arsines continues to attract the attention of investigators. A molecular complex of the type $(Ph_3As)GeClEt$ has been prepared (63). Ali and Harris (64) have studied the reaction between $AsPh_3Cl_2$ with halogens in acetonitrile conductometrically. The stoichiometry of the adducts and the ions formed in solution are shown in the table.

Reactants	Adduct stoicheiometry	Ions in solution
$AsPh_3Cl_2$+ICl	$AsPh_3Cl_3I$	$[AsPh_3Cl][ICl_2]$
$AsPh_3Cl_2$+IBr	$AsBrPh_3Cl_2I$	$[AsPh_3Cl][IBrCl]$
$AsPh_3Cl_2+ICl_3$	$AsPh_3Cl_5I$	$[AsPh_3Cl][ICl_4]$
$AsPh_3Cl_2+I_2$	$AsPh_3Cl_2I_2$	$[AsPh_3Cl][I_2Cl]$
$AsPh_3Cl_2+Br_2$	$AsBr_2Ph_3Cl_2$	$[AsPh_3Cl][Br_2Cl]$

Telluranylidene derivatives of dimedon are dealkylated by triphenylarsine with the formation of the arsomium salt (65).



R = Ph(I), Me(II); E = N, R' = Et; E = P, R' = Ph, Me_3N; E = As, R' = Ph

The enthalpy change which accompanies the formation triphenylphosphine oxide by its oxidation with *tert*-butyl hydroperoxide is -246.17 kJ/Mole. The enthalpy of formation of crystalline Ph_3AsO is 98.7 KJ/mole. The dissociation energy of the As=O bond is 443±25 KJ/mole (66). Trimesitylarsine is oxidized at the platinum electrode by a reversible first wave corresponding to cation radical formation (67). The electron spin spectrum of the radical cation was measured. The data indicated that the upaired electron is localized in a σ-orbital and that the cation radical is monomeric. Hammett substituent constants have been determined for the following group substituents on benzoic acids (68): $(C_2H_5)_2As-$, $(C_2H_5)_2As(S)-$ and $(C_2H_5)_2As(O)-$. In 50 per cent $EtOH{:}H_2O$ the values are: p-$As(C_2H_5)_2$, -0.07; p-$As(O)(C_2H_5)_2$, 0.37; p-$As(S)(C_2H_5)_2$, 0.40; m-$As(O)(C_2H_5)_2$, 0.46; and m-$As(S)(C_2H_5)_2$, 0.44. The vapor pressure has been fitted to an equation of the form (69)

$$\log P = \frac{-A}{T} + B$$

where A = 1998.0 and B = 7.71

An unstable $Et_2O \cdot AsEt_3$ complex is formed between triethylarsine and ethyl ether. Charge transfer complexes which form between iodine and triphenylarsine have been studied in carbon tetrachloride (70) using electrical conductance and refractometry techniques. The data interpreted in terms of the formation of an outer complex, $Ph_3As \cdot I\text{-}I$, and an inner complex, $(Ph_3AsI^+)(I_3^-)$. The vibrational spectra of donor-acceptor complexes of the type $R_3Ga \cdot AsEt_3$ and $R_2GaCl \cdot AsEt_3$ have also been investigated (71). Changes in the metal-carbon bond vibrations as well as other characteristic changes in group frequencies brought about by complexation are also noted. In a related study, Gushikem and Watari (72) studied the vibrational spectra of $R_3As \cdot {}^{10}BX_3$ adducts. The B-As fundamental stretching frequency was assigned between 640 and 740 cm^{-1}. The calculated force constants, 2.84, 2.26, and 1.70 mdyn. $\mathring{A}^{-1}$ show that the B-As bond strength decreases for the adducts in the order $BI_3 > BBr_3 > BCl_3$. The order follows that determined calorimetrically.

X-ray and k-absorption edge spectra of arsenic in Ph_3As and Ph_3AsO were measured (73). The $As^+ \rightarrow O^-$ coordinate bond is predominant over $p_\pi\text{-}d_\pi$ back-bonding.

Hudson and Williams (74) generated radical cations of the type $(Et_3As \mathbin{\dot{-}} AsEt_3)^+$ by gamma irradiation of Et_3As and the electron spin resonance (ESR) spectrum was measured. The spectrum was interpreted in terms of the full 16- line ${}^{75}As$ pattern expected when higher-order effects are important. The electron is largely localized between the two arsenic atoms.

The electrochemical oxidation of Mes_3As (Mes = mesitylene) was studied at the platinum electrode in acetonitrile (75). The first reversible one-electron wave potential gives rise to primary radical cations,

$$Mes_3As \rightleftarrows \underset{\text{blue}}{Mes_3As^{\cdot +}} + e^-$$

The ESR spectrum of the radical cation was measured at room temperature. Line widths, *g* values and hyperfine splittings were reported.

X. *Arsonium Compounds and Arsenic Ylides*

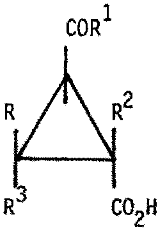
The reaction of methyl aquo-N,N^1-ethylene*bis*(salicylidene iminato) cobalt(III) with tetraphenylarsonium methyl *bis*(dimethylglyoximato)cyanocobaltate(III) gives the cyano bridged complex, tetraphenylarsonium methyl N,N^1-ethylene*bis*(salicylidene iminato) cobalt(III)-μ-cyanomethyl-*bis*(dimethylglyoximato) cobaltate(III) (76). An apparatus for the growth of large crystals, 2 x 2 x 0.5 cm, of phenyltrimethylarsonium TCNQ (radical anion of tetracyanoquinodimethane) has been described by Lenahan and De Pasquali (77). The crystal quality was determined by visual observation, optical microscopy and electron and nuclear magnetic resonance. Triaryltin(IV) compounds undergo reaction with tetraphenylarsonium halides to yield arsonium salts of triaryltin mixed dihalide anions (78,79). The tetraphenylarsonium salt of *tris*(pyridine-2-6-dicarboxylato)uranate(IV)

$$(C_6H_5)_4AsY + R_3SnY \rightarrow (C_6H_5)_4As(R_3SnXY).$$

has been prepared (80) and its ^1H NMR spectrum in d_6-DMSO has been studied. The thermal stability of tetraphenylarsonium permanganate has been investigated (81). Heated in a capillary tube at two degrees/min., this salt explodes violently when the temperature reaches 120-130°C. This compound is of interest because of its potential for the oxidation of alkanes to alcohols and ketones.

Titanium tetrachloride and tetraphenylarsonium azide in methylene chloride yield yellow crystals of $(Ph_4As)[TiCl_4N_3]_2$. The crystal structure of this compound has been determined (82).

Tetraphenylarsonium salts of $[Cl_2SnMe_3]^-$ and $[Cl_2Sn(C_6H_5)_3]^-$ have been prepared (83). A Russian patent (84) describes the preparation of arsonium salts by the electrolysis of tertiary arsines with aromatic or heterocyclic compounds in the presence of NaX on a platinum electrode in acetonitrile. The aromatic or heterocyclic compound furnished the fourth substituent (thenoyl, naphthyl, furyl, pyridyl) and the counter-ion, X^-, by the sodium salt. The reaction between α,β-unsaturated esters and arsoranes of the type $Ph_3A^+ \ ^-CHCOR$, where R = OMe or Ph yields, following estrification, esters of the type shown below (85), where $R = R^2 = R^3 = H$;

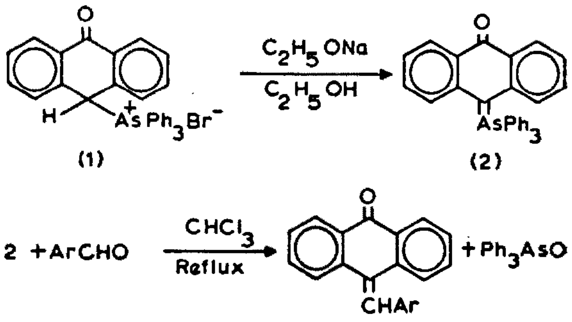


$R^1 = OH$; $R = R^2 = H$; $R^3 = Me$, $R^1 = OH$; $R = R^3 = H$; $R^2 = Me$, $R^1 = OH$; $R = R^2 = R^3 = H$; $R^1 = Ph$; $R^1 = R^2$, $R^3 = H, Me$; $R^1 = Ph$. The kinetics of the decomposition of 10-methyl-10-phenylphenoxarsonium iodide has been investigated (86). In acetone solution only the ion-pair is capable of decomposition.

$$\overset{+}{R_3AsR'} + X^- \rightleftarrows \underset{\text{ion pair}}{\overset{+}{R_3AsR'},\ \overset{-}{X}} \rightarrow R_3As + R'X$$

The equilibrium is virtually quantitatively displaced towards the formation of the arsine and the alkyl iodide.

Tewari and co-workers have published a number of papers on arsonium ylids. 10-Anthronylidenetriphenylarsenane (2, below) is a stabilized arsonium ylid which undergoes condensation with aryl aldehydes to give 10-substituted benzylideneanthrones (4a-j, below) (87).



(1) (2)

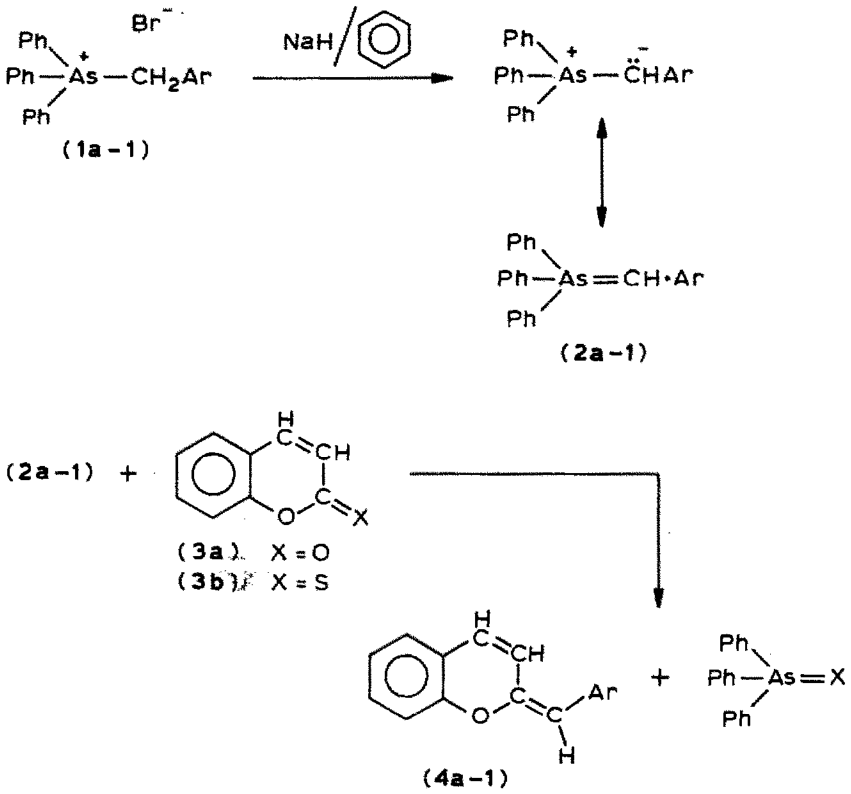
(3a-l) (4a-l)

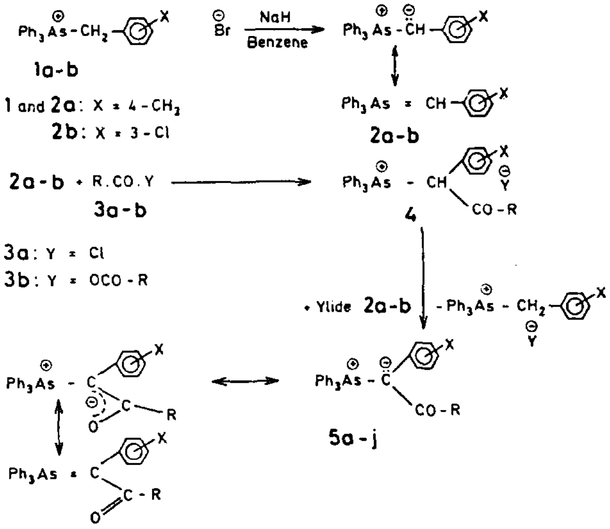
3 and 4: a, Ar = C_6H_5
b, Ar = $3\text{-}NO_2C_6H_4$
c, Ar = $4\text{-}NO_2C_6H_4$
d, Ar = $4\text{-}ClC_6H_4$
e, Ar = $3\text{-}CH_3C_6H_4$
f, Ar = $4\text{-}CH_3C_6H_4$
g, Ar = $4\text{-}CH_3OC_6H_4$
h, Ar = $3,4\text{-}O_2CH_2C_6H_3$
i, Ar = $3,4\text{-diOCH}_3C_6H_3$
j, Ar = $3,4\text{-diOCH}_3\text{-6-Br-}C_6H_2$
k, Ar = $2\text{-}C_4H_3O$
1, Ar = $C_6H_5CH = CH$

Coupling with furfural or cinnamaldehyde was also accomplished successfully, but no reaction took place with ketones such as fluorenone, xanthone or benzophenone. Substituted benzyl bromides undergo reaction with triphenylarsine to give substituted benzylidene triphenylarsonium bromides. Treatment of the latter with NaH/benzene or NaOMe/methanol affords the arsonium ylides, the substituted benzylidenetriphenylarsenanes, Ph_3As =

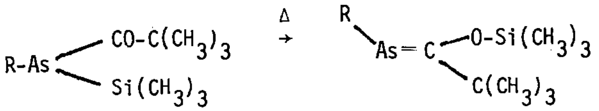
CHAr (88). The reaction of the ylides with cyclic thioketones gives the benzylidene derivatives and triphenylarsine sulfide. For example, with 9-fluorenethione, 9-benzylidene fluorene was obtained. All of the cyclic thioketones employed afforded the same exocyclic olefins. In no case was a thioepoxide obtained. The olefination of lactonyl and lactothionyls through their reactions with arsonium ylides has been described in detail (89). The procedure is outlined below (Scheme 1). The general experimental approach of Tewari has been extended to include the reactions of benzylidenetriphenylarsoranes with acid chlorides or acid anhydrides (90). These yield intermediate arsonium salts which, in the presence of the starting ylides undergo transylidation to carbonyl stabilized arsonium ylides. The overall scheme is shown below.

Scheme 1

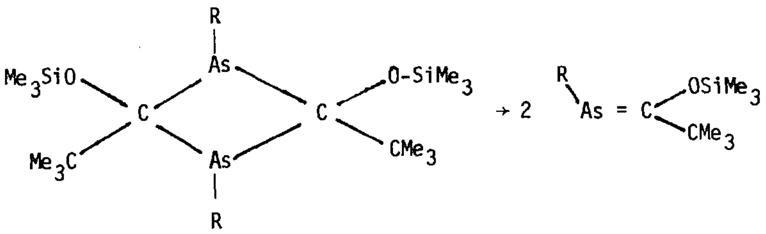

Br⁻
Ph
Ph—As⁺—CH₂Ar
Ph
(1a-1)
NaH/benzene
Ph
Ph—As⁺—C̈H⁻Ar
Ph
Ph
Ph—As=CH•Ar
Ph
(2a-1)
(2a-1) +
H C=CH C=X O
(3a) X = O
(3b) X = S
H C=CH C=C Ar H O
(4a-1)
+
Ph
Ph—As=X
Ph


1a-b
1 and 2a: X = 4-CH₃
2b: X = 3-Cl
NaH
Benzene
2a-b
2a-b + R.CO.Y
3a-b
3a: Y = Cl
3b: Y = OCO-R
4
+ Ylide 2a-b
5a-j

The thermal instabilities of alkyl- and aryl-(2,2-dimethyl proprionyl) trimethylsilyl arsines (below) causes them to rearrange *via* a 1,3-migration of the $(CH_3)_3Si$ group for arsenic to oxygen to form the alkyl and aryl [2,2-dimethyl-1-(trimethylsiloxy)propylidene]propylidene]arsines (91).



1,3-Diarsetanes, on melting, decompose in the manner shown by the following equation.

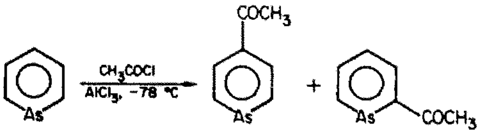


R = Me, Et

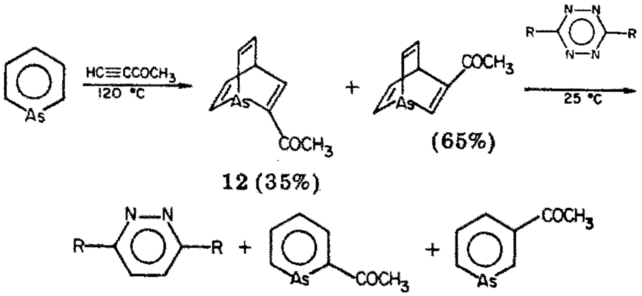
The reaction of phenacyltriphenylarsonium bromide with *N*-methylaniline has been studied (92). The primary product is 2-phenylindole with some 1-methyl-2-phenylindole. The same arsonium salt, with *N,N*-dimethylaniline does not yield any indole. Instead, the nucleophilic substitution product, δ-4'-(dimethylamino)deoxybenzoin is formed. The latter reaction, when carried out in the presence of HBr gives 1-methyl-2-phenylindole.

XI. *Heterocycles Containing Arsenic as a Hetero Atom*

Electrophilic substitution reactions undergone by arsabenzene have been studied (93). At -78°C, in CH_2Cl_2, arsabenzene reacts with 1:1 acetyl chloride-aluminum chloride. Following warming to 25°C prior to hydrolysis, a good yield of 4-acetylarsabenzene is obtained.



2-And 3-acetylarsabenzenes were prepared by a synthetic route which involved the Diels-Alder addition of 3-butyn-2-one to arsabenzene. The isomers shown were formed and their structures were assigned, following separation by GLC, by ^1H NMR spectroscopy.



Treatment of the adducts with 3,6-*bis*(α-pyridyl)-1,2,4,5-tetrazine gave the 2- and 3-acetylarsabenzenes. At -78°C the rates for acetylation of the different positions of arsabenzene are α, 40:β,(< 1):γ,300. All three acetylarsabenzenes are resistant to further Friedel-Crafts reaction conditions.

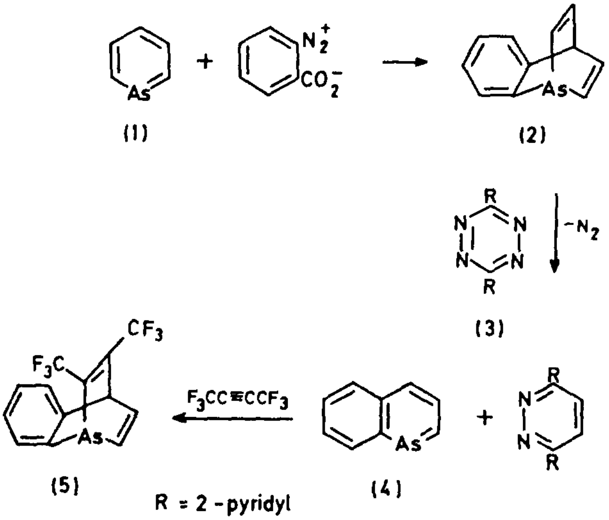
Low yields of nitroarsabenzanes (20%) are possible if the nitration is carried out at 0°C in acetic anhydride. Desilylation of 4-(trimethylsilyl) arsabenzene does not occur under acetylation conditions. Acetylation yields only 2-acetyl-4-(trimethylsilyl)arsabenzene.

The acid-catalyzed deuterium exchange of arsabenzene was studied in CH_2Cl_2/F_3CCOOD. Initial deuteration takes place at the α-position. The results of the deuterium exchange reaction are given in the Table.

Table I. Measured Relative Concentrations (Percent) of Deuterioarsabenzenes for Different Deuteration Conditions

conditions	d_0	d_1	d_2	d_3	d_4
initial	100				
100 °C, 20 h	39.0	46.2 (46.9^a)	14.7	0.2	
100 °C, 3 days	11.0	41.5 (44.3^a)	46.3	1.0	
130 °C, 4 days			59.3	40.6	0.1 (5.3^a)

1-Arsanaphthalene has been synthesized (94). The reaction between arsabenzene and benzenediazonium-2-carboxylate in CH_2Cl_2 gives 1,4-etheno-1,4-dihydro-1-arsanaphthalene (2) (below). The use of a low temperature



acetylene abstraction reagent, 3,6-di(2-pyridyl)-ѕ-tetrazine (3) leads to the formation of 1-arsanaphthalene (4).

Ashe and Chan (95) have measured the pK_a values of arsabenzenecarboxylic acids. The values are listed in the Table. In the same study, they have

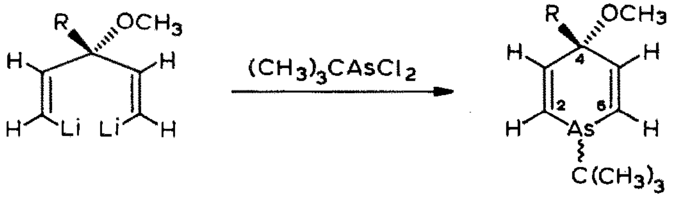
Table 2

pK_a's of Benzoic Acid and Arsabenzenecarboxylic Acids at 20.0 °C with the Derived σ Values

acid	pK_a	σ
benzoic	4.20 ± 0.03	0
2-arsabenzenecarboxylic	3.93 ± 0.03	0.3
3-arsabenzenecarboxylic	3.79 ± 0.03	0.4
4-arsabenzenecarboxylic	(4.10)[a]	0.1

reported dipole moments and charge distributions on the ring atoms of arsabenzenes by CNDO/2, *ab initio*, HMO, and empirical methods. There exist considerable variances among the values calculated by the various methods.

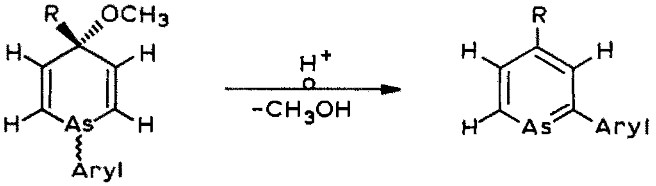
(1Z,4Z)-1,5-dilithio-(3R)-3-methoxy-(1,4)-pentadienes (R = cyclohexyl, $-C(CH_3)_3$, $-C_2H_5$, $-CH_3$, $-C_6H_5$) react with *tert*-butyldichloroarsine to yield the E/Z-isomeric 1-*tert*-butyl-(4R)-4-methoxy-1,4-dihydroarsabenzenes (96).



4 5

4,5	a	b	c	d	e
R	*cyclo*-C_6H_{11}	$C(CH_3)_3$	C_2H_5	CH_3	C_6H_5

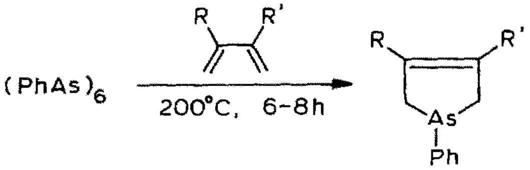
The latter undergo acid-catalyzed loss of the 4-OCH_3 group and the 1-*tert*-butyl group to give the 4-R-arsabenzene. When an aryl group is attached to



the arsenic atom, the acid catalyzed rearrangement gives the 2-aryl-4-R arsabenzene.

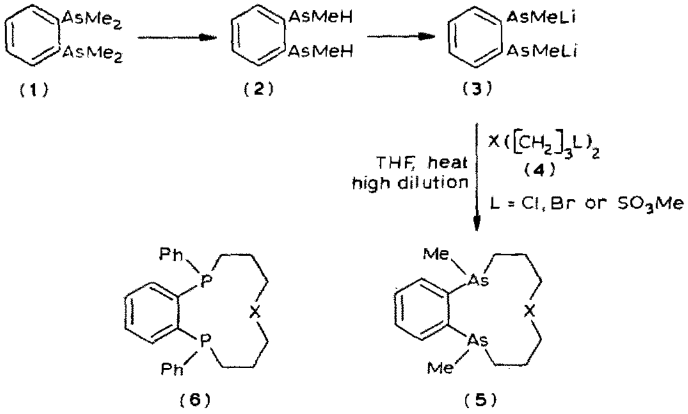
Extensive presentation of ^1H- and ^{13}C-NMR data of compounds of the foregoing types are presented in this paper.

The phenylarsine hexamer, $(C_6H_5As)_6$ reacts thermally with conjugated dienes to yield 2- and 3-arsolenes (arsacyclopentenes) (97).

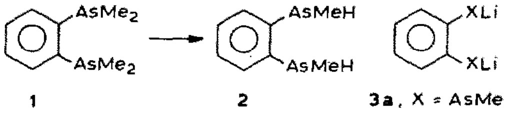

(PhAs)6
R
R'
200°C, 6-8h
R
R'
As
Ph

		Yield	b.p.
1	R = R' = Me	19%	72-73°C/0.3 mmHg
2	R = H, R' = Me	9%	61-62°C/0.3 mmHg
3	R = R' = H	4%	59 60°C/0.6 mmHg

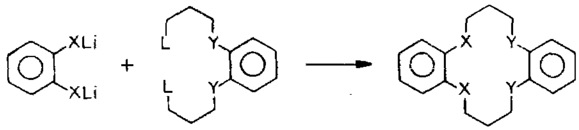
Kyba and co-workers continue their investigation of arsenic-containing macromolecules. Some of these macrocycles are shown in the following schemes (97,98,99):


AsMe2
AsMe2
(1)
AsMeH
AsMeH
(2)
AsMeLi
AsMeLi
(3)
THF, heat
high dilution
X([CH2]3L)2
(4)
L = Cl, Br or SO3Me
Ph
P
X
P
Ph
(6)
Me
As
X
As
Me
(5)

a, X = AsPh
b, X = PPh
c, X = S
d, X = O
e, X = NMe
f, X = NPh


AsMe2
AsMe2
1
AsMeH
AsMeH
2
XLi
XLi

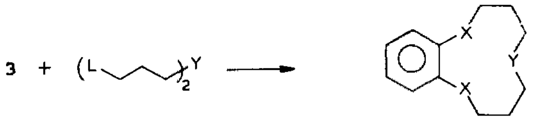
3a, X = AsMe
b, X = PPh



1
a, X = AsMe
b, X = PPh

2
a, Y = O, L = OMs
b, Y = S, L = OMs
c, Y = AsMe, L = Cl

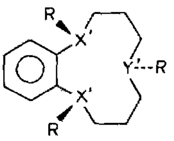
3, X = AsMe, Y = O
4, X = AsMe, Y = S
5, X, Y = AsMe
6, X = PPh, Y = AsMe

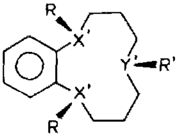


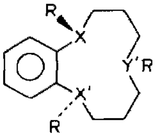
4a, Y = AsPh; L = Br
b, Y = PPh; L = Cl
c, Y = S; L = OMS
d, Y = O; L = OMS
e, Y = NMe; L = Cl
f, Y = AsPh; L = Cl

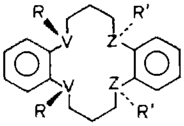
5, AsMe, AsPh
6, AsMe, PPh
7, AsMe, S
8, AsMe, O
9, AsMe, NMe
10, PPh, AsPh

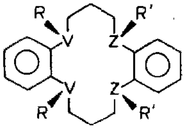
11, PPh, PPh
12, PPh, S
13, PPh, NMe
14, PPh, NPh
15, PPh, O

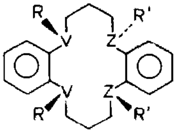

A


B


C


A

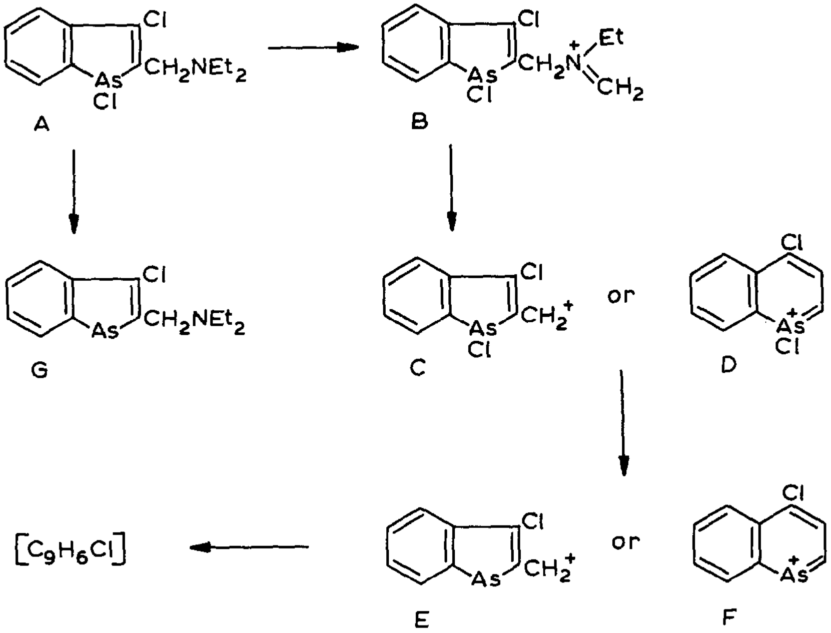

B


C

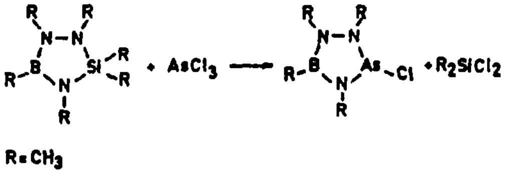
5, VR, ZR' = AsMe
6, VR = PPh, ZR' = AsMe
9, VR, ZR' = PPh

Allen (100) has investigated the ultraviolet and mass spectra of arsindole (benzo[b]arsole) and compared them to those of other group V heterocyclic systems. The molecular fragmentation pattern in interpreted according to Scheme 2.

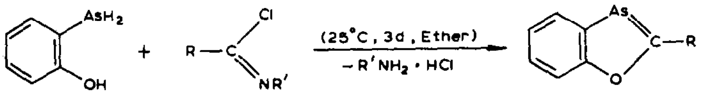
Scheme 2


A
B
C
D
E
F
G
or
or
[C9H6Cl]

Barlos and Nöth (101) have synthesized a triazaarsaborolidine system by the reaction between the triaza-3-sila-5-borolidine and arsenic trichloride.


+ AsCl3
+R2SiCl2
R=CH3

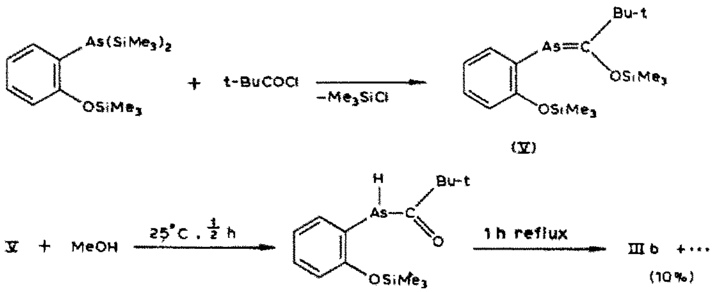
1,3-Benzoxarsoles are prepared by the reaction of hydroxyphenylarsines with imidoyl chlorides (102). The overall reaction is shown as follows


(25°C, 3d, Ether)
– R'NH2 · HCl

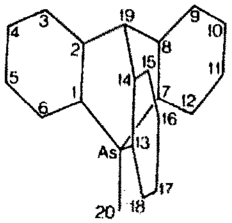
(2)

(IIIa, R = Me;
IIIb, R = t-Bu;
IIIc, R = Ph;
IIId, R = Mes)

A mechanism involving attack at the highly nucleophilic arsenic is proposed.

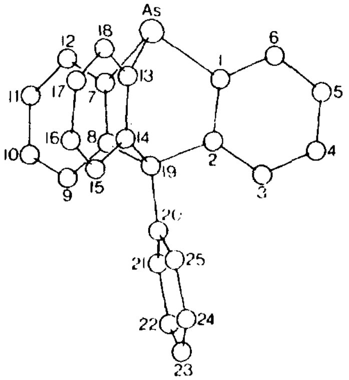

As(SiMe₃)₂
OSiMe₃
+ t-BuCOCl
−Me₃SiCl
Bu-t
As=C
OSiMe₃
OSiMe₃
(V)
V + MeOH
25°C, ½ h
H
As—C
Bu-t
O
OSiMe₃
1 h reflux
IIIb + ...
(10%)

The crystal structures of arsa- and phosphatriptycene have been determined by Freijee and Stam (103). The two compounds are isostructural. They consist of densely packed layers parallel to (10$\bar{1}$) in which the molecular quasi-threefold axes are nearly perpendicular to the layers. Both structures are disordered in the same manner: a fraction of the molecules have As and the bridgehead carbon interchanged. The same laboratory (104) has reported on the crystal structure of 9,10-dihydro-9-methyl-9,10-*O*-benzeno-9-arsonia-anthracene chloride monohydrate (below).


1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
As

Atomic numbering and shape of the molecule.

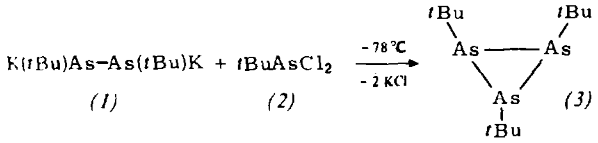
The salient features are as follows: average As-C_{ar} distance is 1.905 (3) Å, the As-CH_3 length 1.883 (8) Å, the average C_{ar}-As-C_{ar} angle is 97.7 (8) and the average C_{ar}-As-CH_3 angle 119.5 (21)°. The crystal structure of 9,10-dihydro-10-phenyl-9,10-*O*-benzeno-9-arsaanthracene has also been determined (105). The shape of the molecule is illustrated. The salient features


As
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

Atomic numbering and shape of the molecule.

are: As-C distances are 1.938 (3), 1.952 (3) and 1.955 (2) A. The average C-As-C angle is 91.5°. Intramolecular steric interaction causes folding of the benzene rings.

An interesting heterocyclic compound, tri-*tert*-butylcyclo-triarsane has been prepared by Baudler and Bachmann (106). The synthesis involves the reaction between 1,2-dipotassium-1,2-di-*tert*-butyl diarsenide and *tert*-butylarsine dichloride.


K(tBu)As–As(tBu)K + tBuAsCl₂
(1)
(2)
-78 °C
-2 KCl
tBu
tBu
As
As
As
tBu
(3)

The colorless crystals melt at 41°C and are stable in the absence of light and air at -30°C. They are soluble in benzene and *n*-pentane. At room temperature they isomerize to (*t*-bu-As)$_4$.

References

1. V.P. Gladyshev, T.V. Syroeshkina, and M.S. Adileva, Tr. Khim.-mettalurg. In-ta AN KazSSR, (29), 108 (1980). CA, 94, 30860.
2. J.L. Wardell, Organomet. Chem., 93, 176 (1980).
3. Y. Shimura, Kagaku (Kyoto), 35(1), 62 (1980).

4. R.G. Goel and W.O. Ogini, Inorg. Chim. Acta, 44, L165 (1980).

5. W. Malisch, M. Kuhn, W. Albert, and H. Rössner, Chem. Ber., 113, 3318 (1980).

6. A.M. Barriola, T.P. Hanusa, and L.J. Todd, Inorg. Chem., 19, 2801 (1980).

7. L.N. Khasrou, Diss. Abstr. Int. B., 41, 2605 (1981).

8. G. Becker, G. Gutekunst and H.J. Wessely, Z. anorg. allg. Chem., 462, 113 (1980).

9. E. Glozbach and J. Lorberth, J. Organometal. Chem., 191, 371 (1980).

10. W. Hoenle and H.G. Von Schnering, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 35B, 789 (1980).

11. L.B. Ionov, A.P. Korovyakov, N.V. Shadrin, and V.A. Shchuklin, Zh. Obshch. Khim., 50, 1893 (1980).

12. M.J.S. Gynane, A. Hudson, M.F. Lappert, P.P. Power, and H. Goldwhite, J. Chem. Soc. Dalton, 2428 (1980).

13. M.J.P. Harger and M.A. Stephen, J. Chem. Soc., Perkin Trans. 1, 705 (1980).

14. F. Kober, Chem.-Ztg., 103, 357 (1979).

15. H.W. Roesky, M. Witt, W. Clegg, W. Isenberg, M. Noltemeyer, and G.M. Sheldrick, Angew. Chem., 92, 959 (1980).

16. K. von Deuten, H. Müller, and G. Klar, Cryst. Struct. Comm., 9, 1081 (1980).

17. H. Fussstetter, G. Kopietz, and H. Noeth, Chem. Ber., 113, 728 (1980).

18. G. Balimann, L.M. Venanzi, F. Bachechi, and L. Zambonelli, Helv. Chim. Acta., 63, 420 (1980).

19. J. Ennen and T. Kauffmann, Angew. Chem., 93, 117 (1981).

20. M.M. Taqui Khan, R. Mohiuddin, M. Ahmed and A.E. Martell, J. Coord. Chem., 10, 1 (1980).

21. R.D. Gigauri, N.I. Gurgenidze, B.D. Chernokal'skii, and Sh. S. Bikeev, Zh. Obschch. Khim., 50, 922 (1980).

22. R.G. Gigauri, B. Chernokal'skii, N.I. Grugenidze, and G.N. Chachava, Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, (10), 101 (1980).

23. B.D. Chernokal'skii and F.R. Garieva, Zh. Obshch. Khim., 50, 1329 (1980).

24. D. Fenske, H. Teichert, H. Prokscha, W. Renz, H.J. Becher, Monatsh. Chem., 111, 177 (1980).

25. E. Lindner and J- P.Gumz, Chem. Ber, 113, 3262 (1980).

26. H.T. Phung, P.B. Chi and F. Kober, Z. anorg. allg. Chem., 466, 179 (1980).

27. R.D. Gigauri, L.I. Goderdzishvili, B.D. Chernokal'skii, M.A. Indzhia, and N.I. Gurgenidze, Soobshch. Akad. Nauk Gruz. SSR, 349, (1980).

28. R.R. Shagidullin, F.D. Yambushev, F.G. Khabitov, L.A. Gorchakova, and A.V. Chernova, Deposited Doc., (1979), VINITI 3813; Chem. Abstr., 94, 102324.

29. R.R. Shagidullin, F.G. Khalitov, F.D. Yambushev, L.A. Gorchakova, and A.V. Grochakova, Deposited Doc., (1979), VINITI 3812; Chem. Abstr., 94, 102324.

30. V.S. Gamayurova, V.I. Savdur, and B.D. Chernokal' skii, Zh. Obshch. Khim., 50, 549 (1980).

31. K. Andrae and W. Gebel, Z. anorg. allg. Chem., 458, 29 (1979).

32. H.G. Ang and W.S. Lien, J. Fluorine Chem., 15, 453 (1980).

33. D. Marchovich and R.E. Tapscott, J. Am. Chem. Soc., 102, 5712 (1980).

34. F.G. Khalitov, R.R. Shagidullin, L.V. Avvakumova, M.M. Aladzhev, and V.S. Gamayurova, Izv. Akad. Nauk SSR, Ser. Khim, 121 (1981).

35. C.D. Baer, J.O. Edwards, M.J. Kaus, T.G. Richmond, and P.H. Rieger, J. Am. Chem. Soc., 102, 5793 (1980).

36. C.D. Baer, J.O. Edwards, and P.H. Rieger, Inorg. Chem., 20, 905 (1981).

37. N.G. Elenkova and R.A. Tsoneva, J. Coord. Chem., 10, 19 (1980).

38. M.I. Kabachnik, Pure Appl. Chem., 52, 859 (1980).

39. M.V. Rosenthal and R.A. Zingaro, Carbohydr. Res., 84, 341 (1980).

40. P. Dehnert, J. Grobe, W. Hildebrandt and D. le Van, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 34B, 1646 (1979).

41. Yu. F. Gatilov and V.A. Perov, Zh. Obshch. Khim., 50, 374 (1980).

42. Yu. F. Gatilov and V.A. Perov, Zh. Obsch. Khim., 50, 374 (1980).

43. Yu. F. Gatilov and V.A. Peroy, Zh. Obsch. Khim., 50, 374 (1980).

44. D.H. Brown, R.J. Cross, P.R. Mallinson, and D.D. MacNicol, J. Chem. Soc. Perkin Trans. 2, 993 (1980).

45. J. Grobe and D. le Van, Z. Naturforsch., B: Anorg. Chem. Org. Chem, 34B, 1653 (1979).

46. P.B. Chi and F. Kober, Z. anorg. allg. Chem., 466, 183 (1980).

47. R. Janta and W. Malisch, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 35B, 1207 (1980).

48. G. Bergerhoff and H. Namgung, Z. Krystallogr., 150, 209 (1979).

49. A.N. Sobolev, V.E. Zavodnik, and V.K. Bel'skii, Int. Semin. Cryst. Chem. Coord. Organomet. Compd., Proc., 3rd. 149 (1977).

50. D.P. Rainville and R.A. Zingaro, J. Organometal. Chem., 190, 277 (1980).

51. S.N. Bhattacharya and M. Singh, Ind. J. Chem., Sect. A, 18A, 515 (1979).

52. R.D. Gigauri, B.D. Chernokal'skii, N.I. Gurgenidze, L.L. Goderdzishvili, and M.A. Indzhiya, Zh. Obshch. Khim, 50, 69 (1980).

53. V.S. Gamayurova, V.K. Gordeev, and B.D. Chernokal'skii, Zh. Obshch. Khim., 49, 2780 (1979).

54. R. Gigauri, L.L. Goderdzishvili, T.N. Shatakishvili, B.D. Chernokal'skii and K. Ya. Burduli, Zh. Obshch. Khim, 50, 2517 (1980).

55. F.L. Tanzella, *Report*, LBL-10478 (Lawrence Berkeley Lab.) (1980). *Res. Abstr.* 5(13) (1980) Abstr. No. 20962.

56. R.L. Kleinberg and L.B. Ebert, Solid State Commun., 37, 437 (1981).

57. K. Barlos, J. Kroner, H. Nöth, and B. Wrackmeyer, Chem. Ber., 113, 3716 (1980).

58. K. Kellner, H-J. Schultz, and A. Tzschach, Z. Chem., 20, 152 (1980).

59. K. Kellner, S. Rothe, E.-M. Steyer and A. Tzschach, Phosphorus and Sulfur, 8, 269 (1980).

60. T.A. Yagudeev, A.N. Nurgalieva, G.M. Dzhakiyaev, and S. Zh. Zhumagaliev, U.S.S.R. 702, 028 (1979).

61. T. Kauffmann, J. Ennen, H. Lhotak, A. Rensing, F. Steinseifer, and A. Woltermann, Angew. Chem., 92, 321 (1980).

62. K. Berghus, A. Hamsen, A. Rensing, A. Woltermann, and T. Kaufmann, Angew. Chem., 93, 116 (1981).

63. O.M. Nefedov, S.P. Kolesnikov, and I.S. Rogozhin, Izv. Akad. Nauk SSSR Ser. Khim., 170 (1980).

64. M. Farhat Ali and G.S. Harris, J. Chem. Soc. Dalton, 1545 (1980).

65. Yu. V. Belkin, N.A. Polezhaeva, V.I. Minkin, and I.D. Sadekov, Zh. Obshch Khim., 50, 907 (1980).

66. V.G. Tsvetkov, Yu. A. Aleksandrov, V.N. Glushakova, N.A. Skorodumova, and G.M. Kol'yakova, Zh. Obshch. Khim., 50, 256 (1980).

67. A.V. Al'yasov, Yu. M. Kargin, E.V. Nikishin, A.A. Vafina, G.V. Ramanov, A. Sh. Mukhtarov, O.V. Parakin, A.A. Kasakova, and A.N. Pudovik, Izv. Akad. Nauk SSSR, Ser. Khim., 189 (1980).

68. A.S. Gel'fond, Yu. G. Galyametdinov, I.P. Ermilova, and B.D. Chernokal'skii, Zh. Obshch. Khim., 50, 559 (1980).

69. A.K. Baev, I.P. Silivanchik, and B.I. Kozyrkin, Zh. Obshch. Khim., 50, 1931 (1980).

70. R. Sahai, P.C. Pande, and V. Singh, Ind. J. Chem. Sect. A, 18A, 217 (1979).

71. A.P. Kurbakova, L.A. Leites, and E.N. Zorina, Koordinat. Khim., 6, 1017 (1980).

72. Y. Gushikem and F. Watari, J. Chem. Soc., Dalton, 2016 (1980).

73. M.C. Shah, B.D. Srivastava, and J. Prasad, Natl. Acad. Sci. Lett. (India), 2, 444 (1979).

74. R.L. Hudson and F. Williams, J. Phys. Chem., 84, 3483 (1980).

75. A.V. Il'yasov, Yu. M. Kargin, E.V. Nikishin, A.A. Vafina, G.V. Romanov, O.V. Parakin, A.A. Kazakova, and A.N. Pudovik, Phosphorus and Sulfur, 8, 259 (1980).

76. K. Dey, R.L. De, and J.K. Bhar, J. Indian Chem. Soc., 56, 1031 (1979).

77. P.M. Lenahan and G. De Pasquali, J. Cryst. Growth, 50, 739 (1980).

78. S.N. Bhattacharya and A.K. Saxena, Ind. J. Chem., 18A, 452 (1979).

79. S.N. Bhattacharya and A.K. Saxena, Ind. J. Chem., 19A, 222 (1980).

80. C. Miyake, H. Sakurai and S. Imoto, J. Inorg. Nucl. Chem., 42, 1725 (1980).

81. B.P. Leddy, M.A. McKervey, and P. McSweeney, Tetrahedron Lett., 21, 2261 (1980).

82. U. Müller, W.M. Dyck, and K. Dehnicke, Z. anorg. allg. Chem., 468, 172 (1980).

83. A.C. Sau, L.A. Carpino, and R.R. Holmes, J. Organometal. Chem. 197, 181 (1980).

84. Yu. M. Kargin, E.V. Nikitin, O.V. Parakin, A.A. Kazakova, Yu. G. Galyametdinov, and B.D. Chernokal'skii, U.S.S.R. 765, 276 (1980).

85. Y-T. Huang, Y-C. Shen, J-J. Ma, and Y-K. Xin, Hua Hsueh Hsueh Pao, 38, 185 (1980).

86. B.D. Chernokal'skii, R.R. Rakhmatullin, and V.I. Gavrilov, Zh. Obshch. Khim., 50, 73 (1980).

87. R.S. Tewari and K. C. Gupta, Indian J. Chem. Sect. B, 17B, 637 (1979).

88. R.S. Tewari, S.K. Suri, and K.C. Gupta, Z. Naturforsch., 35b, 95 (1980).

89. R.S. Tewari, S.K. Suri, and K.C. Gypta, Synth. Commun., 10, 457 (1980)

90. R.S. Tewari and D.K. Nagpal, Z. Naturforsch, 35b, 99 (1980).

91. G. Becker and G. Gutekunst, Z. anorg. allg. Chem., 470, 144 (1980).

92. R.K. Bansal and G. Bhagchandani, Bull. Chem. Soc. Japan, 53, 2423 (1980).

93. A.J. Ashe, III, W-T. Chan, T.W. Smith, and K.M. Taba, J. Org. Chem., 46, 881 (1981).

94. A.J. Ashe, III, D.J. Bellville, and H.S. Friedman, J. Chem. Soc. Chem. Commun., 880 (1979).

95. A.J. Ashe, III and W-T. Chan, J. Org. Chem., 45, 2016 (1980).

96. G. Märkl and R. Liebl, Liebigs Ann. Chem., 2095 (1980).

97. G. Thiollet and F. Mathey, Tetrahedron Lett., 3157 (1979).

97. E.P. Kyba and S-S. P. Chou, J. Chem. Soc. Chem. Commun., 449 (1980).

98. E.P. Kyba and S-S. P. Chou, J. Amer. Chem. Soc., 102, 7012 (1980).

99. E.S. Kyba and S-S. P. Chou, J. Org. Chem., 46, 860 (1981).

100. D.W. Allen, J. Heterocyclic. Chem., 17, 1341 (1980).

101. K. Barlos and H. Nöth, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 35B, 407 (1980).

102. J. Heinicke, B. Raap and A. Tzchach, J. Organometal. Chem., 186, 39 (1980).

103. F.J.M. Freijee and C.H. Stam, Acta Cryst., B36, 1247 (1980).

104. F. Smit and C.H. Stam, Acta Cryst., B36, 1254 (1980).

105. C. van Rooyen-Reiss and C.H. Stam, Acta Cryst., B36, 1252 (1980).

106. M. Baudler and P. Bachmann, Angew. Chem., 93, 112 (1981).