ARSENIC

SURVEY COVERING THE YEARS 1978 AND 1979 [*]

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I. INTRODUCTION

The purpose of this review, which appears periodically, is to cover the recent literature which has been published in the field of organoarsenic chemistry. With few exceptions, we define such compounds as those having at least one arsenic-carbon bond. In this review, those publications are included which have been abstracted in volumes 88, 89, 90, 91 and through no. 18 of volume 92 of *Chemical Abstracts*. Those

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[*] Previous survey see J. Organometal Chem., vol. 176 (1979) p. 245-305.

readers interested in the study of arsines functioning as ligands towards transition metals will not find such coverage included in the present review. As we have previously noted, the number of papers in this field probably exceeds the entire number included in this report. They form part of the literature of transition metal and coordination chemistry. A few unusual ligands and novel coordination compounds are included in this review.

Because both aryl and alkyl derivatives are frequently encountered in published papers, we continue our use of the term *organyl* to include both alkyl and aryl substituents.

Although we noted a dramatic increase in the number of papers concerned with environmental and biochemical aspects of organoarsenic compounds in our last two reviews, only a small number appear to have been published during the past two years. This is probably not due to a lack of interest, but may more likely reflect a shift to biological, ecological, nutritional, and toxicological studies. A large number of publications in these areas may not appear in *Chemical Abstracts*. The most obvious increase in numbers is to be noted in the field of heterocyclic organoarsenic compounds. Arsabenzene has attracted a great deal of investigative effort.

The authors wish to express once again their appreciation to the Robert A. Welch Foundation of Houston, Texas and the Center for Energy and Mineral Resources of Texas A&M University for financial support during the preparation of this review.

II. REVIEWS, BOOKS, AND REPORTS

The annual surveys dealing with organoarsenic chemistry have been published for the years 1975-77 [1,2]. The great increase in interest in heterocyclic arsenic compounds is reflected in the relatively large number of reviews, along with a book, which have appeared. A 233 page book entitled *Arsenheterocyclen* has been authored by Tzschach [3]. Atkinson [4] has published a review on six-membered heterocycles containing arsenic, and Russian authors [5] have reviewed the steric structure of heterocyclic arsenic compounds. Ashe [6] has published a review entitled *The Group 5 Heterobenzenes* and Indian authors have published a 43 page review on the recent developments in the chemistry of cyclic arsines [7].

Diorganylarsino-alkali metal derivatives, R_2AsM, M=Li, Na, K, are ably presented in a report by Tzschach and Voigtländer [8] which discusses the preparation, reactions, and properties of these compounds. Organoarsenic compounds are discussed extensively in one of the recent volumes of the Houben-Weyl series [9]. Chernokal'skii and co-authors [10] have reviewed the effect of substituents on the reactivity of organoarsenic compounds. Russian authors have presented reviews on the reactivity of tertiary arsine sulfides [11] and on the stereochemistry of organoarsenic compounds [12]. Duncan [13], and Doak, et al. [14], have published reviews on arsenic compounds. Those investigators interested in the biological fate of arsenicals will enjoy the review written by Frederick Challenger [15], one of the real pioneers in this field of research.

Finally, reviews on arsenic ylides [16] and on the dynamic stereochemistry of arsines [17] have also been published.

III. ARSINES AND POLYARSINES

A very large number of papers concerned with transition metal complexes in which arsines function as donor ligands with π-acceptor properties continue to be published. The reader is reminded that the coverage of this aspect of the literature is not included in this review.

The reaction between lithium cyclopentadienide and $(Me_3C)_2AsCl$ in tetrahydrofuran at -70° gives the sigma bonded derivative, $C_5H_5As(CMe_3)_2$ [18]. The electrochemical reduction of aromatic arsonic acids gives the arsines in 65-75% yields [19]. Thus, *o*-methoxyphenyl-, *o*-hydroxyphenyl-, and *o*-aminophenylarsines were prepared by the electrochemical reduction of the corresponding arsonic acids. The electrochemical oxidation of aromatic and aliphatic arsines in acetonitrile has been studied by Russian investigators [20].

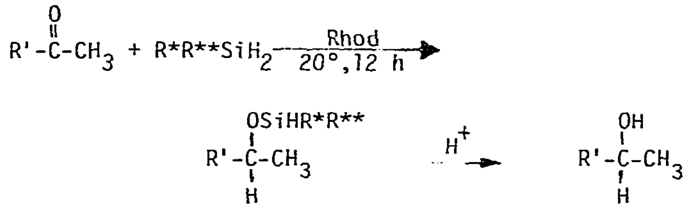
The organoarsenic polymer - $(CH_3As)_x$ - *bis*[catena-poly(methylarsenic)] has been the subject of several investigations. Lewis and Rheingold [21] have studied the low frequency dielectric response of this material. The dielectric relaxation behavior at excitation frequencies below 10 Hz is highly anomalous. They have examined their results in terms of Jonscher's *universal* dielectric response. The band structure of this material has been investigated [22]. It was reported that the energy gap of this solid is determined by the delocalization of the electrons of the 4*p* atomic orbitals of the arsenic atoms. Both forms of the polymer were studied, i.e., those with and without alternation in the As-As bond lengths in the solid. Tyutyulkov [23] has carried out an extended Hartree-Fock calculation (LCAO approximation with Hubbard's model Hamiltonian) of the form of the solid without alternation of the bond lengths. The width of the energy gap is claimed to have a purely correlative character. In the one-electron approximation the width of the energy gap is zero irrespective of whether, or not, the geometry of the lattice is taken into account.

IV. TRIORGANYL ARSINES

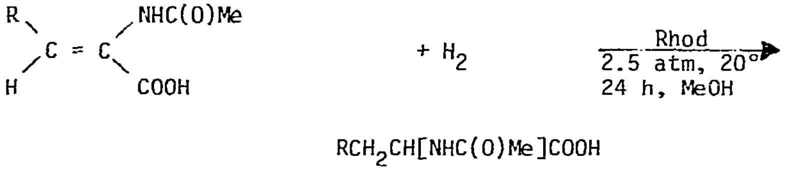
Bis(*p*-ethylphenyl)arsines have been studied by Russian workers [24]. The preparations are quite straightforward. Thus, the reaction of $p\text{-}EtC_6H_4MgBr$ with As_4O_6 gives $[(p\text{-}EtC_6H_4)_2As]_2O$. The latter when treated with HCl gives $(p\text{-}EtC_6H_4)_2AsCl$ which undergoes reaction with RMgX (R = Me, Et, Pr, Me_2CH, and Bu) to give the desired arsine. Arsineacetylenic alcohols and aldehydes are the subject of a paper by Kuz'min and co-workers [25]. The Grignard reaction of $R_2AsC \equiv CBr$ with CH_2O, oxirane, methyloxirane, and Me_2NCHO followed by hydrolysis gives $R_2AsC \equiv CCH_2OH$ (R = Et, Pr, Bu, pentyl, hexyl, phenyl), $R_2AsC \equiv CCH_2CH_2OH$, $R_2AsC \equiv CCH_2CH(OH)Me$, and $R_2AsC \equiv CCHO$, respectively.

A similar report by Gigauri and co-workers [26] describes the preparation of dialkyl(α-naphthyl) arsines.

Calhoun, et al., [27] have synthesized (+)- and (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-*bis*(diphenylarsino)butane (diarsop). The ligand was prepared by the reaction between 1,4-ditosyl-2,3-O-isopropylidene-D-threitol with diphenylarsenide dioxanate. The white, air stable crystals of (+)-diarsop melt at 68-69°. The rhodium complex bearing this ligand, diarsop-$[Rh(C_8H_{12})Cl]_2$ (Rhod), functions as an asymmetric catalyst in the hydrogenation of α,β-unsaturated acids and the asymmetric reduction of ketones, as illustrated by the equations which follow.

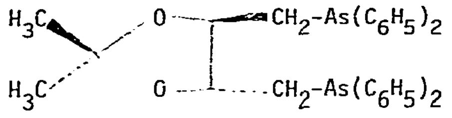


$$R'\text{-}\overset{\overset{\Large O}{\|}}{C}\text{-}CH_3 + R^{*}R^{**}SiH_2 \xrightarrow[20°, 12\ h]{Rhod} R'\text{-}\underset{H}{\overset{OSiHR^{*}R^{**}}{C}}\text{-}CH_3 \xrightarrow{H^+} R'\text{-}\underset{H}{\overset{OH}{C}}\text{-}CH_3$$



$$(R)(H)C{=}C(NHC(O)Me)(COOH) + H_2 \xrightarrow[\substack{2.5\ atm,\ 20° \\ 24\ h,\ MeOH}]{Rhod} RCH_2CH[NHC(O)Me]COOH$$

Roberts and Wild [28] have successfully resolved the disymmetric chelating agent (RR,SS)-*o*-phenylene-*bis*(methylphenylarsine) into its enantiomers. This was accomplished by the fractional crystallization of the internally diastereoisomeric palladium complexes containing the ditertiary arsine and optically active *ortho*-metallated dimethyl(α-methylbenzyl)amine. Related to investigations in the field of asymmetric catalysis, Murrer, et al., [29] have described an improved synthesis of *trans*-4,5-*bis*[diphenylarsinomethyl]-2,2-dimethyl-1,3-dioxolan. This arsine, TBDA, is shown below.



TBDA

Kauffmann and co-workers [30] have prepared diphenylarsinomethyllithium and used this compound, through its reaction with alkyl iodides, to extend the length of alkyl substituent. The reactions are illustrated by the following equations.

$$(Ph_2As)_2CH_2 \xrightarrow[\text{THF, -40°}]{\text{BuLi}} Ph_2AsCH_2Li$$

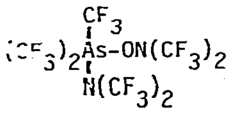
$$Ph_2AsCH_2Li + I(CH_2)_3CH_3 \longrightarrow Ph_2As(CH_2)_3CH_3$$

Poly-4,4'-diarsabiphenylene has been prepared and described by Herrmann and Scheel [31]. The compound was prepared by the reduction of biphenylene-4,4'-diarsonic acid with hypophosphoric acid. The solid state reaction between poly-4,4'-diarsabiphenylene and elemental selenium gives glasses having the stoichiometry $Se_{100-3x}(BpAs_2)_x$, where Bp is biphenylene. Ang and Lien [32] have investigated the reaction between perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) and *tris*(trifluoromethyl)arsine. The reaction proceeds as follows:

$$n(CF_3)_2NON(CF_3)_2 + (CF_3)_3As \longrightarrow [(CF_3)_2N]_nAs(CF_3)_{3-n}$$

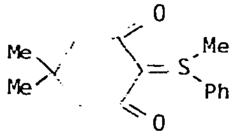
$$n = 1,2 \qquad\qquad + n(CF_3)_2NOCF_3$$

Free radical mechanisms were eliminated. The most probable mechanism involves the formation of a pentacovalent intermediate:

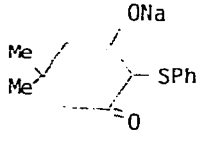


$$(CF_3)_2\overset{\overset{CF_3}{|}}{\underset{\underset{N(CF_3)_2}{|}}{As}}-ON(CF_3)_2$$

Compounds of type I, shown below, treated with Ph_3As or Et_2AsPh in the presence of $NaBPh_4$ undergo dealkylation to compounds of type II [33]. The arsenic compound is converted to $MeR_2As^+PhBPh_4^-$.



I



II

Tewari and Chaturvedi [34] have utilized triphenylarsine to accomplish a facile synthesis of 4-acetylstilbenes. The procedure involves the preparation of the triphenylarsorane derivative, $H_3CC(O)C_6H_4CH = AsPh_3$, which undergoes reaction with an aromatic aldehyde to yield a stilbene.

Shulman [35] has studied the kinetics of the oxidation of group Va compounds by *tert*-butyl hydroperoxide. The reaction under study is

$$R'OOH + R_3M \longrightarrow R'OH + R_3M = O$$

$$M = P,\ As,\ Sb$$

The oxidations were studied polarographically. For a series of compounds $(C_6H_5)_3M$, M = As, P, Sb, the reactivity with the hydroperoxide followed the order $(C_6H_5)_3P \geq (C_6H_5)_3Sb > (C_6H_5)_3As$. The reaction was mechanistically interpreted in terms of a series of nucleophilic attacks on a soft electrophile. The anomalous order of the triphenylstibine was attributed to the increased availability of the *d* orbitals in this compound for π-bonding to periodic oxygen.

The ionization constants have been measured for a series of arsinobenzoic acids, $RR'AsC_6H_4COOH$ [36]. The pKa values varied over a relatively narrow range from 9.70 to 10.10. The only large deviation was for the derivative R = Et, R' = Cl, *m*-benzoic acid for which the pKa was 2.88. Arsines form hydrogen bonds to benzyl alcohol and phenols. The results of a study by Mendel and Kolbe [37] are reported in the table below.

Donor	Acceptor	$-\Delta H$(kcal. mol.$^{-1}$)	$-\Delta S$(e.u.)	$\Delta\nu_{OH}$(cm^{-1})
benzyl alcohol	n-Pr_3As	0.0	0.8	113
benzyl alcohol	i-Pr_3As	0.5	2.5	122
phenol	i-Pr_3As	1.5	5.4	215
phenol	Cy_3As	1.6	5.7	227

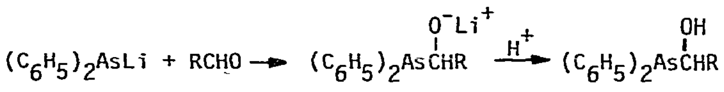
A number of studies on the infra-red and Raman spectra of arsines have been published. Demuth, Apel, and Grobe [38,39] have studied the gas phase i.r. and liquid phase Raman spectra of $CF_3As(CH_3)_2$ and $(CF_3)_2AsCH_3$ and carried out normal coordinate analyses. Crocker and Goggin [40] have utilized i.r. and Raman studies to establish the preferred conformations in AsR_3, R_3 = Me_3, Et_3, Me_2Et and $MeEt_2$. In the solids, the preferred conformations have the C-Me groups *gauche* to the lone pair of the central atom. Kurbakova [41] has reported similar studies for Et_3As. The Et_3As crystal contains only one conformer, TTT or GGG. The vibrational spectrum of triallylarsine has been studied by Davidson and Phillips [42]. The internal vibrational modes of the allyl groups in $As(CH_2\text{-}CH = CH_2)_3$ was assigned in terms of a local symmetry, C_s, with non-interacting allyl units. The skeletal $As(C\text{-}C)_3$ modes required the assumption of an overall molecular symmetry of C_3, with all the allyl groups in the *gauche*-conformation.

Fluorine-19 n.m.r. measurements have been performed on *m*- and *p*-fluorophenylarsines by Van der Kelen and co-workers [43]. The ^{19}F chemical shift parameters provide evidence that the d_π-d_π interaction between a trivalent As ligand and a metal carbonyl moiety is non-zero. Wilkie [44] has determined the spin-lattice relaxation times for all carbons in triphenylarsine. The *o*-, *m*-, and *p*-carbons all relax exclusively by a dipole-dipole mechanism. The α-carbons relax predominantly by the dipole-dipole mechanism below about 40°C while the spin-rotation mechanism is most important above this temperature. The preferred solution conformations in solution, and rotational barriers of the phenyl moiety in 3,5-dichlorobenzyl dimethylarsine has been investigated [45]. The long range spin-spin coupling constants between the methylene protons and the ring protons were measured. The couplings over six bonds were used to derive internal barriers to rotation about the carbon-carbon bond to the phenyl ring. This barrier is about 3.0 ± 0.5 kcal. $mol.^{-1}$ in the arsine. The conformation of lowest energy is that in which the H_2C-X bond lies in a plane perpendicular to the benzene plane.

Several other physico-chemical investigations involving triorganylarsines have been reported. Baev, et al., [46] have measured the enthalpy of dissociation of $Me_3Ga \cdot AsEt_3$ and found it to be 14.6 kcal. $mol.^{-1}$ while the entropy of dissociation is 34.6 e.u. Smirnov and co-workers [47] have studied the photoionization of $(C_6H_5)_3M$, where M = P, As or N. In ethanol, irradiation at 4.2-90 K led to photoionization. At the lowest temperatures solvated electrons were formed, but with increase in temperature, radicals from the matrix were formed. The photoionization efficiency decreased as the atomic number of M increased. The UV-irradiation of triphenylarsine in single crystal form is reported in the doctoral dissertation of W. T. Cook [48]. The irradiation results in the formation of $[(C_6H_5)_2As\cdot]$ radicals. Finally, the fusion diagram of the Me_3Ga-Et_3As system has been investigated [49].

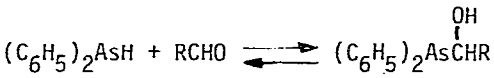
V. COMPOUNDS HAVING METAL-ARSENIC BONDS

Alkali metal-arsenic bonded derivatives have found a number of synthetic applications. Busse, et al. [50], have reported on the reactions of diphenyllithioarsine and diphenylarsine with aldehydes. Diphenyllithioarsine reacts with aldehydes to form lithium salts of α-hydroxyalkylarsines,



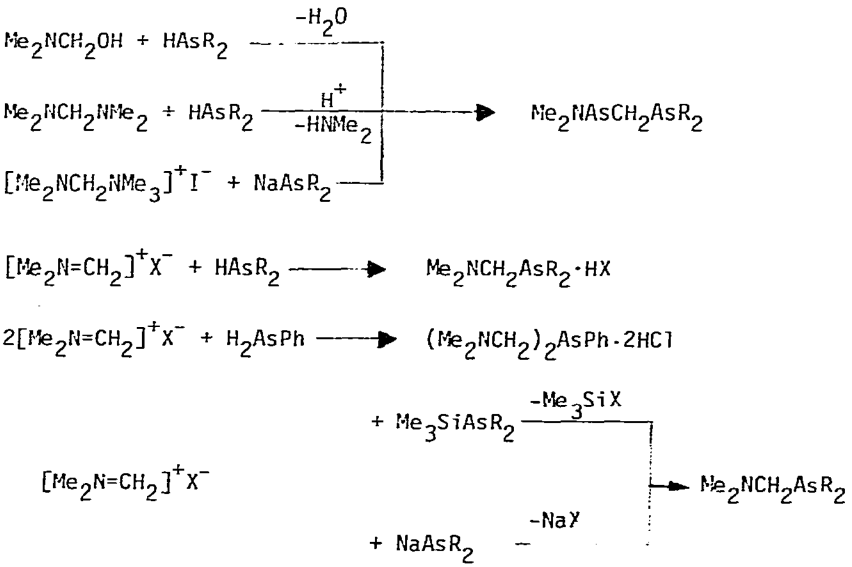
$$(C_6H_5)_2AsLi + RCHO \longrightarrow (C_6H_5)_2As\overset{O^-Li^+}{\overset{|}{C}}HR \xrightarrow{H^+} (C_6H_5)_2As\overset{OH}{\overset{|}{C}}HR$$

Diphenylarsine reacts with aldehydes below room temperature in the absence of solvents to produce white solids. This reaction is catalyzed by acids. By NMR spectral analysis, both ^{1}H and ^{13}C, the products were identified as diphenyl(α-hydroxyalkyl)arsines. These compounds are thermally unstable and in organic solvents the following equilibrium exists,



$$(C_6H_5)_2AsH + RCHO \rightleftharpoons (C_6H_5)_2As\overset{OH}{C}HR$$

α-Dialkylaminomethylarsines have been prepared [51] by several methods, including the use of sodium-arsenic derivatives. The reactions used are summarized below.



$$Me_2NCH_2OH + HAsR_2 \xrightarrow{-H_2O} Me_2NAsCH_2AsR_2$$

$$Me_2NCH_2NMe_2 + HAsR_2 \xrightarrow[-HNMe_2]{H^+} Me_2NAsCH_2AsR_2$$

$$[Me_2NCH_2NMe_3]^+I^- + NaAsR_2 \longrightarrow Me_2NAsCH_2AsR_2$$

$$[Me_2N{=}CH_2]^+X^- + HAsR_2 \longrightarrow Me_2NCH_2AsR_2\cdot HX$$

$$2[Me_2N{=}CH_2]^+X^- + H_2AsPh \longrightarrow (Me_2NCH_2)_2AsPh\cdot 2HCl$$

$$[Me_2N{=}CH_2]^+X^- + Me_3SiAsR_2 \xrightarrow{-Me_3SiX} Me_2NCH_2AsR_2$$

$$[Me_2N{=}CH_2]^+X^- + NaAsR_2 \xrightarrow{-NaY} Me_2NCH_2AsR_2$$

In the reaction with the silane, $X^- = Cl^-$, while in the reaction with the dialkylarsenide, the ease of reaction follows the order $I^- > Br^- > Cl^-$. Issleib, Balszuweit and Thorausch [52] have investigated the effects of reaction conditions on the metallation of phenylarsine with *n*-butyllithium or alkali metals. The monometallated compound, M(H)AsPh (I) can undergo hydrogen elimination with formation of the metallated diarsine, PhAs(M)-As(M)Ph (II). The observations reported by these investigators are given in the table.

Formation of I and II from PhAs H_2 with *n*-Butyllithium or Potassium

Reactants	Molar ratio	Solvent	Temp. °C	Reaction time	Product I	Product II
$PhAsH_2/LiBu$	1:1	ether	-60	1h	92.9	7.1
$PhAsH_2/LiBu$	1:1	ether	-45	1h	85.0	15.0
$PhAsH_2/K$	1:1	dioxane	102	9h		100.0
$PhAsH_2/K$	1:1.1	dioxane	102	2h		100.0

Heinicke and Tzschach [53] have prepared imidoylarsines according to the following reaction:

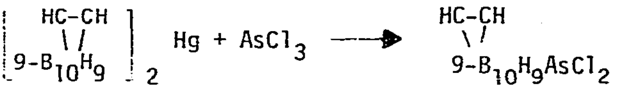
$$RPhAsLi + ClC(:NR^1)R^2 \longrightarrow RPhAsC(:NR^1)R^2.$$

Metal arsenides have been reported [54] to react with *vic*-dihalides to give acetylenic compounds of the type $Ph_2AsCH_2C{\equiv}CCH_2AsPh_2$ in low yields.

The reaction of sodium [undecahydro-5,6-dicarba-*nido*-decaborate] with arsenic trichloride and zinc dust in refluxing diethyl ether was found to give a low yield of arsacarbaborane, $B_8C_2{}^{7,8}As^9H_{11}$. It is isolated as an air-stable crystalline solid. Mass spectral and ^{11}B NMR spectra were reported for this compound [55]. Russian investigators [56,57] have prepared compounds containing a B-As bond by the reaction between a carboranylmercury compound and arsenic trichloride,

$$(C_2H_2B_{10}H_9)_2Hg + AsCl_3 \longrightarrow (C_2H_2B_{10}H_9)AsCl_2$$

A similar report [58] describes the reaction of 9-(*o*-carboranyl)- and 9-(*m*-carboranyl)mercury with arsenic trichloride in $C_2H_4Cl_2$ to give 9-(*o*-carboranyl)- and 9-(*m*-carboranyl)dichloroarsine. These are described as air and thermally stable and containing a B-As σ-bond.



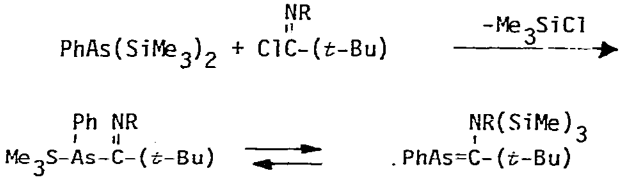
$$\left[\overset{\text{HC-CH}}{\underset{9\text{-}B_{10}H_9}{\backslash /}}\right]_2 Hg + AsCl_3 \longrightarrow \overset{\text{HC-CH}}{\underset{9\text{-}B_{10}H_9AsCl_2}{\backslash /}}$$

Compounds containing a thallium-arsenic bond have been described by Walther and Bauer [59]. These were prepared by the reaction between trialkylthalliums and an arsine.

$$R_3Tl + HAsR^1R^2 \longrightarrow R_2Tl\text{-}AsR^1R^2 + RH$$

In the place of the trialkylthallium, dialkylthallium dimethylamides can also be used.

Heinicke and Tzschach [60] have reported the preparation of As = C derivatives by the reaction of phenyl*bis*(trimethylsilyl)arsine with pivaloyl imidechlorides. The iminoacylsilylarsines rearrange to *N*-silylated As = C isomers according to a temperature dependent equilibrium.



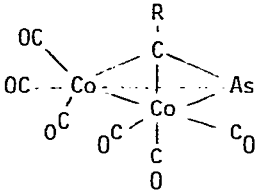
$$PhAs(SiMe_3)_2 + \overset{\text{NR}}{\overset{\|}{\text{ClC}}}\text{-}(t\text{-}Bu) \xrightarrow{-Me_3SiCl}$$

$$Me_3S\text{-}\overset{\text{Ph}}{\overset{|}{\text{As}}}\text{-}\overset{\text{NR}}{\overset{\|}{\text{C}}}\text{-}(t\text{-}Bu) \rightleftarrows .PhAs{=}\overset{\text{NR(SiMe)}_3}{\overset{|}{\text{C}}}\text{-}(t\text{-}Bu)$$

Arsenic-tin bonding has been reported by Du Mont [61]. When triethylphosphinedichlorostannylene, $Et_3P\text{-}SnCl_2$ was allowed to react with an equimolar amount of di-*tert*-butyl(trimethylsilyl)arsine at 0° in toluene, di-*tert*-butylarsino(chloro)tin(II) was isolated from the reaction mixture: $Sn(Cl)\text{-}As(t\text{-}Butyl)_2$.

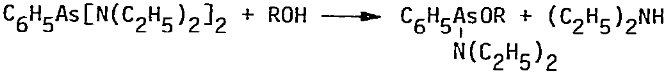
Nelson [62], citing As-As bond distances in molecules such as $Co_2[(CO)_5P(C_6H_5)_3]As_2$, has discussed the existence of As = As double bonds. Cawley [63] has written on the rotameric abundances of diarsines as estimated by photoelectron spectroscopy. From such measurements, *tetrakis*(trifluoromethyl)diarsine is estimated to be 100% *trans*, while tetramethyldiarsine is 12% *gauche* and 88% *trans*.

A Co-As-C bond has been reported by Seyferth and Merola [64] in dicobalt hexacarbonyl complexes of the type shown below. Röttinger and Vahrenkamp [65] have synthesized the molecule $[(CO)_3Fe\text{-}AsCH_3]_4$. This molecule is built around a cubane-like structure containing As-Fe-As bonds.



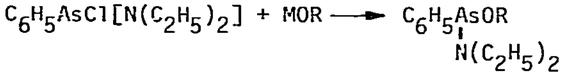
VI. COMPOUNDS HAVING ARSENIC-NITROGEN BONDS

Ionov and co-workers [66] have reported the preparation of arsines that bear an As-O, As-C, and As-N bond by the reaction between *bis*(diethylamino)phenylarsine and a mole of alcohol. Such derivatives



$$C_6H_5As[N(C_2H_5)_2]_2 + ROH \longrightarrow C_6H_5\underset{N(C_2H_5)_2}{\underset{|}{As}}OR + (C_2H_5)_2NH$$

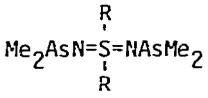
can also be prepared by the reaction between phenyldiethylaminoarsine chloride and an alkali metal alkoxide in benzene.



$$C_6H_5AsCl[N(C_2H_5)_2] + MOR \longrightarrow C_6H_5\underset{N(C_2H_5)_2}{\underset{|}{As}}OR$$

Connell [67] has incorporated both As(III) and As(V) into an octaethylporphyrin ring. The complexes are reported to be ionic with the trivalent arsenic atom displaced from the plane of the porphyrin ring. Electronic and emission spectra were recorded for the complexes. Fluorescence and phosphorescence quantum yields and experimental triplet lifetimes were measured for the pentavalent species. The trivalent species displayed no detectable fluorescence.

Azides having the structure Me_2AsN_3 have been prepared by Mueller [68]. The compounds exhibit a temperature dependent exchange of the azido group on the NMR time scale. Wolfsberger and Försterling [69] have prepared some interesting N,N'-*bis*(arsino)-S,S-dialkylsulfodiimides. These were

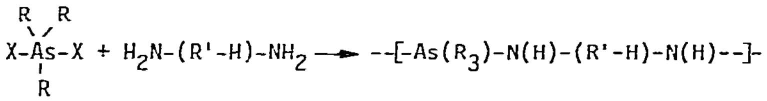


$$Me_2AsN{=}\overset{R}{\underset{R}{S}}{=}NAsMe_2$$

synthesized by the reaction between S,S-dialkylsulfodiimides and chlorodimethylarsine.

$$R_2S(=NH)_2 + 2R'_2AsCl \longrightarrow R_2S(=NAsR'_2)_2$$

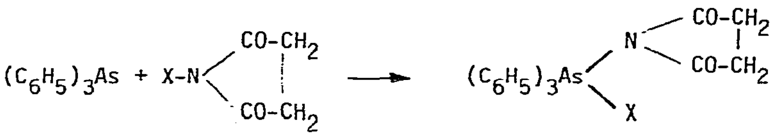
Arsenic(V) polypyrimidines have been prepared by the reaction between triorganylarsenic dihalides and diamines in organic solvents in the presence of a base [70]. A typical reaction is shown as follows.



$$X\text{-}\overset{R\ R}{\underset{R}{As}}\text{-}X + H_2N\text{-}(R'\text{-}H)\text{-}NH_2 \longrightarrow \text{--}[\text{-}As(R_3)\text{-}N(H)\text{-}(R'\text{-}H)\text{-}N(H)\text{--}]\text{-}$$

The polymers formed displayed weight averages of *ca*. 4000 and were characteristic semirigid organometallic polymers. The polymers inhibit the growth of *Ps. fluorescens*.

The addition of N-haloamides to triorganylarsines yields triorganylarsinoamidohalides [71].

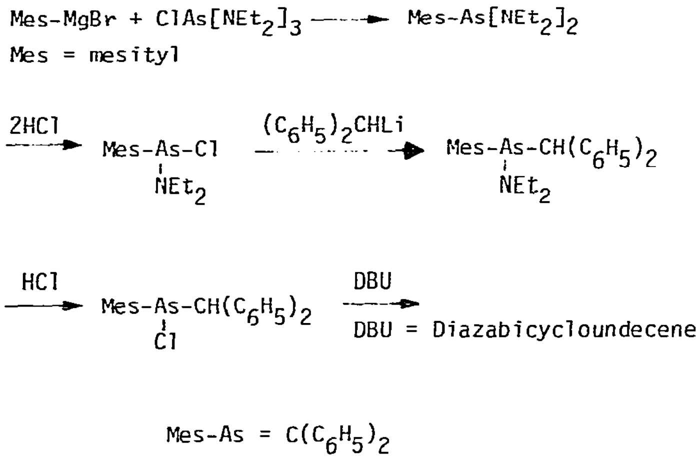


Tris(dialkylamino)arsines undergo reaction with sulfur dioxide to give the arsine oxide. Thus, at 30°, the following reaction takes place [72].

$$2As(NR_2)_3 + SO_2 \longrightarrow 3(R_2N)SO + As_2O_3$$

Japanese workers [73] have investigated substituent effects in the reaction of diethylaminodialkylarsines with ethylene carbonate. The rate was found to vary according to the class of alkyl substituent on the arsenic atom in the order: secondary alkyl>primary alkyl>methyl. Correlations with the Taft equation were good and the σ^* value was calculated to be positive.

Mesityl(diphenylmethylene)arsane has been prepared by Klebach and co-workers [74]. The reaction sequence is shown below.



$$\text{Mes-MgBr} + \text{ClAs[NEt}_2]_3 \longrightarrow \text{Mes-As[NEt}_2]_2$$

Mes = mesityl

$$\xrightarrow{2HCl} \text{Mes-}\underset{\text{NEt}_2}{\text{As}}\text{-Cl} \xrightarrow{(C_6H_5)_2CHLi} \text{Mes-}\underset{\text{NEt}_2}{\text{As}}\text{-CH}(C_6H_5)_2$$

$$\xrightarrow{HCl} \text{Mes-}\underset{\text{Cl}}{\text{As}}\text{-CH}(C_6H_5)_2 \xrightarrow{DBU}$$

DBU = Diazabicycloundecene

$$\text{Mes-As} = \text{C}(C_6H_5)_2$$

mesityl(diphenylmethylene)arsane

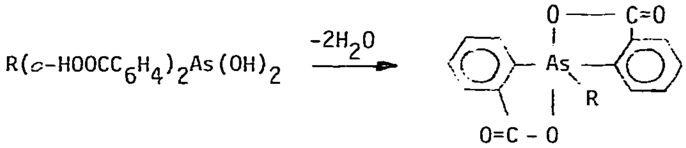
Analogues of S_4N_4, *viz.*, $Ar_2As_2S_2N_4$, where Ar = phenyl or mesityl have been synthesized according to the following reaction [75].

$$2ArAsCl_2 + 2Me_3SiNSNSiMe_3 \longrightarrow Ar_2As_2S_2N_4 + 4Me_3SiCl$$

The aryl groups are bonded to the arsenic atoms, each of which, in turn, is bonded to two nitrogen atoms. A sulfur atom bonds each of two nitrogen atoms. Thus, the structure is represented by a boat-shaped, eight-membered ring. The crystal structures of the two derivatives are reported. The ring is conformationally similar to the S_4N_4 cage. H-bonded complexes involving $R_2AsNR'_2$(I), Et_2NR(II) and R_3As(III) as donors have been compared [76]. The donor molecules were C_6H_5OH, C_2H_5OH and $ClCH_2COOH$. The electron-donor properties decreased in the order II>>I>III.

VII. COMPOUNDS HAVING ARSENIC-OXYGEN BONDS

The oxidation of triorganyl arsines by hydrogen peroxide or permanganate has been reported on by Gigauri and co-workers [77]. The most commonly formed oxidation product is the arsine oxide, R_3AsO. When an alkyl substituent is present on an aromatic substituent, permanganate oxidation results in the simultaneous oxidation of the alkyl substituent as well as the arsenic. For example, *tris*(*o*-tolyl)arsine is converted to *tris*(*o*-carboxyphenyl)dihydroxyarsorane. Dehydration of alkyl*bis*(*o*-carboxyphenyl)arsine oxides gives rise to cyclic structures of the type illustrated by the equation which follows.



Arsinous acid esters are easily hydrolyzed and readily undergo the following hydrolytic reaction [78].

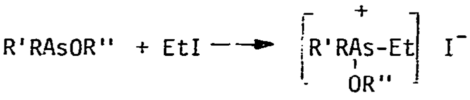
$$2RR'AsOR'' + H_2O \longrightarrow (RR'As)_2O + 2R''OH$$

Chromatographic investigation reveals the presence of a number of components on the column. The components present, and their formation, are interpreted in terms of the following equilibria:

$$2R_2AsOR \rightleftharpoons R_3As + RAs(OR)_2$$

$$3RAs(OR)_2 \rightleftharpoons R_3As + 2As(OR)_3$$

Valiullina and Chernokal'skii [79] have carried out a kinetic study of the reaction of arsenic(III) esters with ethyl iodide. The first stage of the reaction is postulated as a nucleophilic attack either by the arsenic atom (1), or the oxygen atom (2) on the carbon atom of the alkyl halide,

(1) 

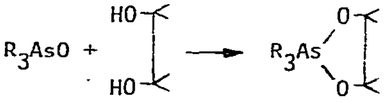
$$R'RAsOR'' + EtI \longrightarrow \left[R'R\underset{OR''}{As}-Et\right]^{+} I^-$$

(2) 

$$R'RAsOR'' + EtI \longrightarrow \left[R'RAs\underset{R''}{O}-Et\right]^{+} I^-$$

Interpretation of the kinetic data leads to the conclusion that first stage of the reaction is represented by course (1).

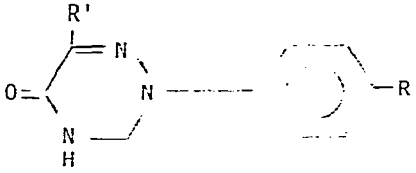
The reaction between nitroethane and ethyloxarsine, *bis*(diethyl)arsinous anhydride and diethyl ethylarsonite has been studied [80]. At 100-120°, in the absence of solvent and in an atmosphere of argon, the As-C bond is broken. As_2O_3 is isolated in yields of 30-50%. Nitroethane, when heated with $EtAs(OEt)_2$ also yields ethanol and ethyl acetate, as determined by GLC and the ^1H NMR spectrum. Ionov, et al., [81] by the reaction between $C_6H_5AsEtCl$ and MeOH or EtOH in the presence of brucine, claim to have isolated the optically active ester of an arsinous acid, $(+)-C_6H_5AsEt(OR)$. The oxidation of arsines by ozone has been investigated by Yambushev and co-workers [82]. In this study, a series of chiral arsine oxides, specifically, alkylarylarsinylbenzoic acids was synthesized. Arsines were oxidized by ozone, permanganate, and hydrogen peroxide. The oxidation mechanisms are discussed. The condensation of arsine oxides with *vic*-diols yields cyclic esters [83]. This reaction is outlined below,



The reaction is carried out in benzene with the water formed during the reaction being removed by azeotropic distillation. All of the examples given utilize triphenylarsine oxide. The oxidation of diarylalkylarsines by hydrogen peroxide yields the arsine oxides [84]. Thus, R(*m*-$MeC_6H_4)_2As$ is converted to the oxide by H_2O_2. The oxide, with HX (X = Br, Cl), gives the salts, [*m*-$MeC_6H_4)_2AsR(OH)^+]X^-$. A series of arsinic acid esters was prepared by direct esterification of the acids by alcohols [85],

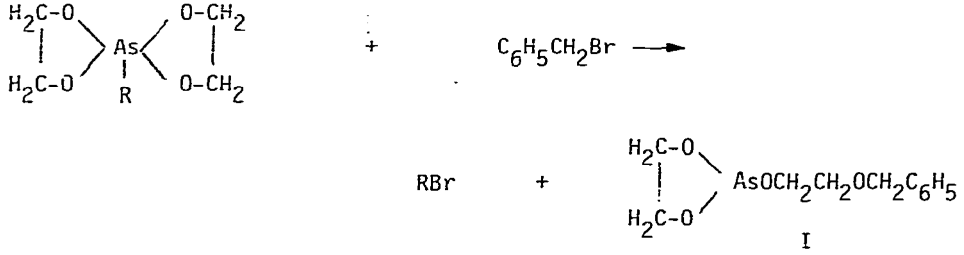
$$R_2As(O)OH + R'OH \longrightarrow R_2As(O)OR' + H_2O$$

Some of the physico-chemical measurements carried out on these esters included ^1H NMR, infra-red, and potentiometric titrations. Arsenic derivatives of 6-azauracil have been described by Czech workers [86]. These have the structure shown below, where R is $As(O)(OH)_2$ and



R' is CN. The synthetic procedure involved the cyclization of *p*-$[(HO)_2As(O)]C_6H_4NN{=}C(CN)CO(NHCOOEt)$ and $NCCH_2CONHCO_2Et$.

Several other publications in the field of cyclic esters of arsenic have appeared. Benzyl bromide reacts with spiroarsoranes to ultimately form *tris*[2-(benzyloxy)ethyl] arsenite, as proposed in the following reaction scheme [86a].

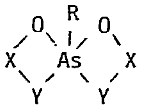


$$I + C_6H_5CH_2Br \longrightarrow BrAs(OCH_2CH_2OCH_2C_6H_5)_2$$

II

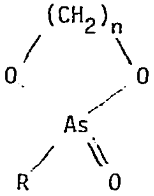
$$3\ II \rightleftharpoons 2As(OCH_2CH_2OCH_2C_6H_5)_3 + AsBr_3$$

The reaction was studied by heating the spiroarsorane and benzyl bromide in sealed ampoules and fractionating the mixture. The fractions were analyzed by ^1H NMR and elemental analysis. Mallon and Wieber [87] have prepared spirocyclic thioesters and ester amides of orthoarsonic acids. These have the structure illustrated below. These were prepared by the

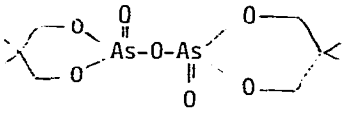


R = Me, C_6H_5; X = CH_2CH_2, *o*-C_6H_4, 2,3-$C_{10}H_6$; Y = S, NH, NMe

reaction between $C_6H_5As(O)(OH)_2$ or $MeAs(OMe)_4$ with HOXYH. Dale and Frøyen [87a], prepared 2-oxo-1,3,2-dioxarsenanes (below) by allowing



acyclic arsonates, $R\text{-}AsO(OCH_3)_2$ to react with a 1,3-diol. The reactions were carried out in carbon tetrachloride. When R = OCH_3, and As-O-As bonded compound of the type

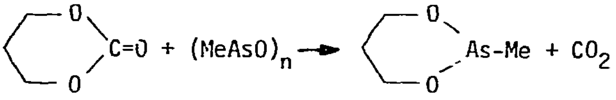


was formed. A number of other synthetic techniques were employed, but they were found to give the spirocyclic compounds. Wunderlich [88] has determined the crystal structure of 2-methyl-2,2'-spirobi(1,3,2-benzodioxaarsole). The geometry of the pentacoordinate As atom is described as a 74 per cent rectangular pyramid with the methyl group in the apical position. The molecule contains *trans*-basal angles O-As-O of 158.6 and 143.1° and apical-basal angles C-As-O of 108.6, 108.3, 100.2 and 101.1°. H_3AsO_3, H_3AsO_4 and $(CH_3)_2As(O)OH$ were treated with a variety of trimethylsilation reagents. They are converted to $As(OSiMe_3)_3$, $OAs(OSiMe_3)_3$, and $(CH_3)_2As(OSiMe_3)_3$, respectively [89]. The most effective silylating reagent is N,O-*bis*(trimethylsilyl)trifluoroacetamide in dimethylformamide. These derivatives can be separated on a gas chromatograph; columns of OV-225 coated on Gas-Chrom Q (100-120 mesh) were most effective for separation of the three species. The analytical detection limits were 0.1 ng of injected As(V) and $(CH_3)_2As(O)OH$ and 1 ng of injected As(III).

A number of papers on the preparation metal salts and on the liquid-liquid extraction of metal ions from aqueous phases have appeared. The oxidation of $(C_6H_5)_3As$ to the oxide is catalyzed by Fe(III). Thus, at increased temperatures, the complexes, $FeCl_3[(C_6H_5)_3AsO]_{1.5}$ and $FeCl_3[(C_6H_5)_3AsO]_2$ were separated from the system $FeCl_3$-$(C_6H_5)_3As$-MeCN [90]. A general study of metal arsonate hydrates having the formula $M(C_6H_5)AsO_3 \cdot H_2O$ has been reported by Cunningham, Hennelly, and Deeney [91]. M in these salts is Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd, in the +2 state. The study includes preparative procedures, thermogravimetric analyses, X-ray powder diffraction studies, diffuse reflectance spectra, measurements of the magnetic moments, some ESR measurements, and Mössbauer spectroscopy of the iron salts. Refluxing nickel(II) acetate with an arylarsonic acid yields polymeric $RC_6H_4AsO_3Ni$, where R = *p*-Me, *p*-Cl, *p*-Br, *o*- and *p*-MeO, *o*-COOH, and *o*-NO_2. All the salts have an octahedral structure except for R = *o*-NO_2 which has a distorted tetrahedral structure [92]. Tin(IV) nitrate oxidizes triphenylarsine [93]. Thus, in carbon tetrachloride solution, triphenylarsine undergoes reaction with tin(IV) nitrate to give $[(C_6H_5)_2AsO_2]_2Sn(NO_3)_2$. These compounds were studied by a variety of physico-chemical techniques including ^{119m}Sn Mössbauer spectroscopy. It is suggested that the compounds have polymeric structures involving bridging arsonate groups and unidentate nitrate groups which gives rise to a six-coordinate tin atom. Dibenzyltin compounds of the type $RC_6H_4AsO_3Sn(CH_2C_6H_5)_2$ where R includes a variety of aromatic ring substituents have been reported [94]. They are described as insoluble polymeric solids in which the tin is six-coordinate. Molybdo(organoarsonates) are the subject of a dissertation by Rajkovic-Blazer [95]. Complexes of the type $R_2AsMo_4O_{15}H_2^-$, $(RAs)_2Mo_6O_{24}^{4-}$, $(RAs)_2Mo_6O_{25}H_2^{4-}$ and $(RAs)_4Mo_{12}O_{46}^{4-}$ were synthesized and characterized. Electronic, vibrational and NMR spectral studies were carried out. Single crystal X-ray structure determinations also became available during the course of the study.

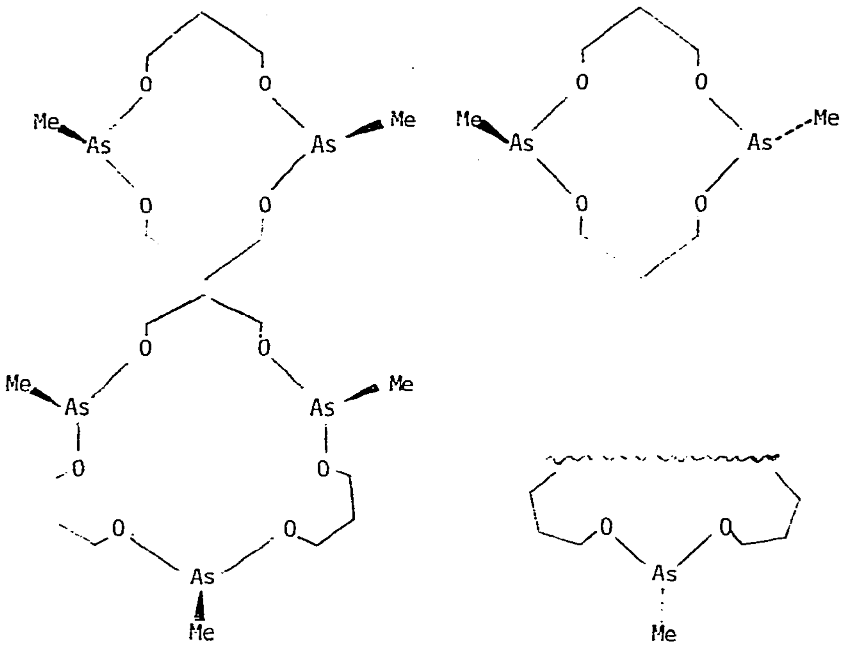
Arsenate esters, $OAs(OCH_2C_6H_5)_3$ are the subject of a dissertation by Kaus [96]. The crystal structure of the title compound was determined and it was found to be isostructural with tribenzyl phosphate. There appears to be less d-p π-bonding in the arsenate than in the phosphate. The alcohol exchange reaction was investigated by ^1H NMR line-broadening. In acetonitrile, the exchange reaction appears to proceed *via* a five-coordinate transition state. The relative basicities of R_3AsX, where X = O, S, or Se towards protonation have been measured potentiometrically [97]. In nitromethane, the basicities were found to decrease in the order $R_3AsO > R_3AsS > R_3AsSe$.

French workers [98], using ^1H and ^{13}C NMR spectroscopy as a tool, have investigated the preferred conformations of methyl-2 dioxa-1,3 arsa-2 cyclohexanes. The compounds for study were synthesized either by condensation of a diol with $RAsX_2$, where X = Cl or NMe_2, or by the reaction between a cyclic carbonate and methylarsine oxide,

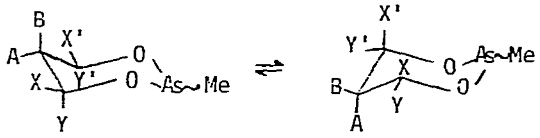


I

Only a single isomer of I, based on the As-Me resonance was observed. However, the compounds shown below displayed two isomeric forms.



The following conformational equilibrium was studied and all coupling



constants were measured. A number of other related systems were investigated. Geoffrey and Llinares [99] have irradiated single crystals of sodium dimethylarsinate with X-rays to produce $CH_3(O)As(O^-)CH_2$ and $(CH_3)_2AsO_2^=$. The ESR spectra of irradiated species were investigated as a function of temperature. The $\bar{g}$ tensors and hyperfine coupling constants were measured at 105, 165, 215, and 295°K. The identity of the radical species was made through these measurements. The influence of temperature and ambient oxygen on the nature of the radicals formed by the irradiation of the crystals was also investigated. Howard and Tait [100] have studied the ESR spectra of four coordinate arsenic radicals. They conclude that four-coordinate arsenic radicals react with molecular oxygen to give peroxy radicals. Because of the broadness of the observed lines, hyperfine coupling with As was not resolved.

In CCl_4 solution, tertiary arsine oxides form hydrogen bonded complexes with phenol. The enthalpy of this reaction increases in the following sequence [101],

$$(C_6H_5)_3AsO < (C_6H_5)_2AsO\text{-}n\text{-octyl} < (C_6H_5)AsO\text{-}(n\text{-octyl})_2 < (n\text{-octyl})_3AsO < (cyclo\text{-}C_6H_{11})_3AsO$$

A similar study [102] was concerned with hydrogen bond formation between $(C_6H_5)_3AsO$ and haloacetic acids. In work of a closely related type [103], the isotherms (aqueous-dichloroethane or benzene) for the extraction of nitric acid by various arsine oxides was investigated. Complexes of the type $R_3AsO\cdot(HNO_3)_i$, where i = 1,2,3,4 are reported. The first mole of acid extracted transfers its proton so as to form $R_3AsOH^+....NO_3^-$. Tertiary arsine oxides in water-immiscible organic solvents have been tested as extractants for U(VI), Pu(IV,VI) and Np(IV,VI) from their aqueous solutions in nitric acid [104]. A study very closely related to those just described is concerned with the extraction of nitric acid from its aqueous solutions by arsine oxides [105].

Bravo and Laurent [106] have prepared and characterized BF_3 adducts of the following types: $(RO)_3AsO\cdot BF_3$ and $R'(RO)_2AsO\cdot BF_3$. ^1H, ^{11}B and ^{19}F NMR spectra of the compounds were measured. The J^1_{BF} coupling constant in $Me(EtO)_2AsO\cdot BF_3$ is 22.0 Hz. This is to be compared with $J^1_{BF} = 15$ Hz in free BF_3.

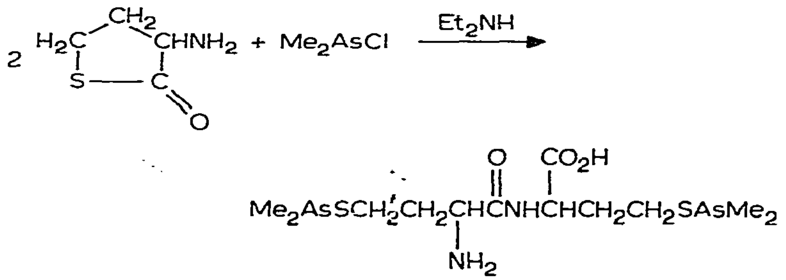
The differential pulse polarography of phenylarsine oxide has been investigated [107]. Its use as a titrant in the indirect determination of Cl and O_3 is described. The technique is useful in the analysis of water and wastewater. The electrical conductivities of a number of dichlorotriorganoarsoranes, R_3AsCl_2, in nitrobenzene and in acetone have been measured [108] over the concentration range $2 \times 10^{-2} - 10^{-5}\underline{M}$. The electrical conductivities are interpreted in terms of the following equilibria:

$$[R_3AsCl_2]_2 \rightleftharpoons [R_3AsCl^+] + [R_3AsCl_3^-] \rightleftharpoons 2[Cl^-,R_3AsCl^+] \rightleftharpoons 2Cl^- + 2R_3AsCl^+$$

The concentrations of the solute species depend on the solute concentration.

VIII. COMPOUNDS HAVING ARSENIC-SULFUR OR ARSENIC-SELENIUM BONDS

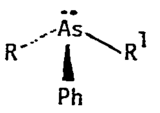
Compounds of the type $RSAsR'_2$ and $RSeAsR'_2$ are the subject of two dissertations. Daniel [109] has synthesized and studied the physical properties of derivatives in which R is galactose while Velazquez-Rosenthal [110] has carried out similar studies in which R is glucose or arabinohexose. The syntheses of dimethylarsinous acid esters of 1- and 6-thiogalactose are reported by Daniel and Zingaro [111]. *S*-dimethylarsino derivatives of 6-mercaptopurine, cysteine, penicillamine, homocysteine, glutathione α-dihydrolipoic acid and the S- and Se-dimethylarsino derivatives of thio- and selenocholesterol have been synthesized [112]. The synthesis of *bis*[*S*-(dimethylarsino)homocysteine] was carried out directly from the thiolactone as shown in the following equation



$$Me_2AsSCH_2CH_2\underset{NH_2}{CH}\overset{O}{\overset{\|}{C}}NH\overset{CO_2H}{CH}CH_2CH_2SAsMe_2$$

A number of these compounds show carcinostatic activity, *in vivo*, in the P388 test system.

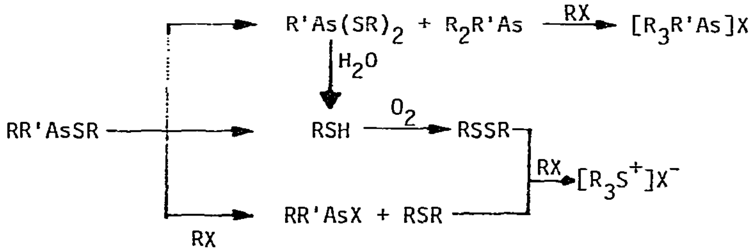
Optically active esters of thioarsinous acids have been reported [113]. They have the structure shown below.



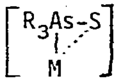
R = Me, Et, Me_2CH, Me_3C; R^1 = EtS, PrS, BuS, $C_5H_{11}S$

The compounds were prepared by the reaction between RPhAsX (X = halogen) and the mercaptan in the presence of optically active $Et_2NCHMePh$. When (+)-$MeC_5H_{11}PhAs$ was made to undergo reaction with PrMgBr, (-)-MeAsPhPr was formed. Abalonin, et al. [114] have investigated the reaction of triorganylarsine sulfides with alkylhalides. The reaction is very complex and a variety of different products are formed. The reaction, based upon the products identified, can be represented as follows:

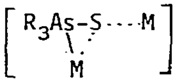
$$R_2R'AsS + RX \rightarrow [R_2R'AsSR^+]X^- \longrightarrow RR'AsSR + RX$$



Arsine sulfides are reduced to the arsines by the following metals [115]: Hg, Na, Cu, Ag. The metals are converted to the metal sulfides. The following types of intermediates, involving nucleophilic attack by the metal at the electrophilic arsenic, are proposed:



divalent metal

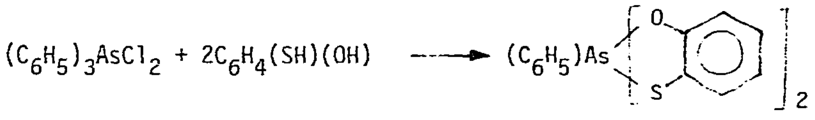


univalent metal

The reaction between $(C_6H_5)_3As$ and SeS_2 in benzene yields $(C_6H_5)_3AsSe\cdot(C_6H_5)_3AsS$ [116]. The product is formulated as a solid solution of the respective chalcogenides. In an attempt to learn more about the action of phenyl radicals on tertiary arsine sulfides, the photochemical and thermochemical reactions of diethylphenylarsine sulfide with diphenylmercury have been investigated [117]. Photolysis of these compounds in benzene yielded HgS, diethylphenylarsine, and biphenyl. The same products are formed in the thermolysis of diethylphenylarsine sulfide with diphenylmercury. The nature of the products formed suggests that the phenyl radicals do not react with the arsine sulfide. Instead, they react with one another, or with the solvent. The reaction is interpreted in terms of an oxidation-reduction with mercury. The latter forms from diphenylmercury.

$$Et_2C_6H_5AsS + Hg \longrightarrow HgS + Et_2C_6H_5As$$

The reaction of triphenylarsine dichloride with *o*-mercaptophenol proceeds in the following manner [118]:



The reaction between tetramethyldiarsine and *bis*(trifluoromethyl) disulfide gives dimethyl(trifluoromethylthio)arsine [119]:

$$Me_2As\text{-}As\ Me_2 + CF_3SSCF_3 \longrightarrow 2Me_2AsSCF_3$$

The reaction between $Hg(SeCF_3)_2$ with $AsBr_3$ and CS_2 gives the arsenic-selenium bonded derivative, $As(SeCF_3)_3$ [120].

Crystal structure determinations of a number of compounds having an arsenic-sulfur bond have been carried out. Triphenylarsine sulfide [121] is isomorphous with $(C_6H_5)_3PS$ and $(C_6H_5)_3PSe$. The As = S bond distance is 2.082 Å and is essentially a double bond. One of the phenyl rings lies almost coplanar with the As-S bond while the others have an average torsion angle of 53°. In $(C_2H_5)_3AsS$ [122], the As-S bond distance is 2.114 A. The As-S bond distances in (dimethyldithiocarbamato)-iodomethylarsenic(III) are 2.329 and 2.348 Å [123]. The crystal structure of trichloro[1,3-dimethyl-2(3H)-imidazolethione]arsenic(III) has been reported [124]. In this case, the As-S bond distance is 2.301 Å.

In the latter two cases, the much longer As-S bond distances are a reflection of the much lower As-S bond orders.

Arsenic(III) halides and arylarsenic(III) dihalides form adducts with thiourea(T). A number of thioureas was investigated. All of the adducts exhibited a 1:1 stoichiometry. All of the adducts decompose on exposure to atmospheric moisture at varying rates (Cl>>Br; $AsX_3\cdot T > ArAsX_2\cdot T$). A variety of physico-chemical measurements including infra-red, Raman and ^1H NMR were reported [125]. Trigonal-bipyramidal structures are proposed for these adducts.

An infra-red and Raman study of triethylarsine sulfide has been carried out in the solid and liquid state, in several solvents and at various temperatures [126]. In the solid state, Et_3AsS possesses C_3 symmetry with the three ethyl groups being *gauche*-oriented with respect to the As-S bond. In solution and in the molten state, three isomers possessing C_2, C_s and C_3 symmetries are present. The electrical conductivities of a number of alkylthiotriorganylarsonium salts in acetone have been measured [127]. The salts studied have the formulation $[R_3AsSR']^+X^-$, where R = cyclohexyl, phenyl, ethyl, and R' = ethyl or methyl. The greatest conductivities are observed for X = fluoborate followed by X = methyl sulfate and then iodide. When X = bromide, the salts are strongly associated in solution. The ^{75}As NQR spectra of several aryldiethylarsine sulfides have been measured [128]. In the group of compounds studied, the ^{75}As NQR frequencies are below those measured previously for four-coordinate arsenic compounds. This implies that all four single bonds around the arsenic are equivalent. The ^{75}As NQR frequencies were correlated with the Hammett substituent constants.

IX. COMPOUNDS CONTAINING ARSENIC-HALOGEN (HALOGENOID) BONDS

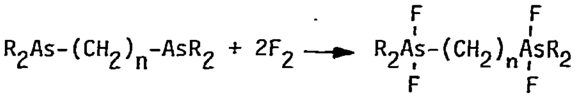
The hydrolysis of *bis*(*p*-chlorophenyl)arsenic chloride by aqueous sodium hydroxide gives *bis*(*p*-chlorophenyl)arsinous anhydride, m.p. 149-150° [129].

$$2(p\text{-}ClC_6H_4)_2AsCl + 2NaOH \rightarrow [(p\text{-}ClC_6H_4)_2As]_2O + 2NaCl + H_2O$$

Bis(*m*-tolyl)arsenic chloride undergoes reaction with potassium cyanide in the absence of solvent to yield the cyanide, $(m\text{-tolyl})_2AsCN$. In acetone, refluxing with potassium thiocyanate yields $(m\text{-tolyl})_2AsSCN$ [130].

The reaction of pentachlorophenyl lithium with $AsCl_3$ gives only $(C_6Cl_5)_2AsCl$, even in the presence of a large excess of the lithium reagent [131]. Treatment of $(C_6Cl_5)_2AsCl$ with chlorine yields a residue which hydrolyzes rapidly to $[(C_6Cl_5)_2As]_2O$. Chiral arsinous acid esters have been prepared by the reaction between a diorganylarsenic chloride and an alcohol in the presence of an optically active amine [132]. Thus, the reaction between methylphenylarsenic chloride and ethanol in ether at -35° in the presence of (-)-N,N-diethyl-α-methylbenzylamine yields a mixture which is highly enriched with respect to (+)-ethyl methylphenylarsinite. Several other examples of such partial asymmetric syntheses are given. When phenyl- and phenylalkylarsines, $As(C_6H_5)_3$, $CH_3As(C_6H_5)_2$, $C_2H_5As(C_6H_5)_2$, $CH_2[As(C_6H_5)_2]_2$ and $CH_3C[CH_2As(C_6H_5)_2]_3$ react with HBr in non-aqueous solvents, the phenyl-arsenic bonds are selectively cleaved yielding $AsBr_3$, CH_3AsBr_2, $C_2H_5AsBr_2$, $CH(AsBr_2)_2$ and $CH_3C(CH_2AsBr_2)_3$. The mass fragmentation patterns of these compounds are reported in some detail. Fragments containing As-As bonds or As_3 clusters are involved [133].

Triphenylarsine difluoride, m.p. 134-136°, is conveniently prepared by the reaction between triphenylarsine oxide and hydrogen fluoride in boiling water [134]. The difluoride precipitates from the solution and can be recrystallized from acetone. Elemental fluorine adds to methylene or polymethylene bridged diarsines to yield the pentavalent, fluorinated arsenic(V) compounds [135].



$$R_2As\text{-}(CH_2)_n\text{-}AsR_2 + 2F_2 \longrightarrow R_2\overset{F}{\underset{F}{As}}\text{-}(CH_2)_n\overset{F}{\underset{F}{As}}R_2$$

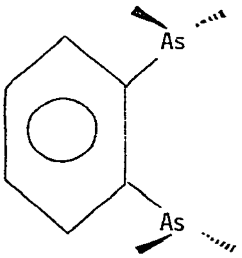
Elemental fluorine also adds to a diphenylalkylarsine or triphenylarsine to yield the difluoride. Tri(pentafluorophenyl)arsine has been prepared and some of its reactions have been investigated [136]. Because it has a very limited tendency to coordinate, isolation of compounds such as neutral $O_3ClOAgAs(C_6F_5)_3$ and the cationic $Ag[(C_6F_5)_3As]_2ClO_4$ is possible. Reaction with Cl_2 or $TiCl_3$ yields $(C_6F_5)_3AsCl_2$. Metathetical reactions of the latter with silver salts give monosubstituted derivatives $(C_6F_5)_3AsClX$, where X is NO_3^-, ClO_4^- or OH^-. Alcoholysis by ROH, R = Me, Et, or C_6H_5 gives $(C_6F_5)_3AsCl(OR)$. Interhalogens, XY, add to R_3As to form R_3AsXY [137]. Exchange reactions of R_3MIY, Y = Cl, Br, with KNCO, AgNCO or KNCS gives R_3MIZ, Z = NCO, NCS.

Ethylstibine and CH_3AsCl_2 undergo rapid hydrogen-chlorine exchange followed by the slow elimination of HCl to form the all arsenic ladder homopolymer $(CH_3As)_x$ [138]. No antimony or ethyl group incorporation in $(CH_3As)_x$ was detected nor were any other solid products formed.

$$C_2H_5SbH_2 + 2CH_3AsCl_2 \longrightarrow C_2H_5SbCl_2 + 2CH_3AsCl$$

$$CH_3AsCl \longrightarrow (CH_3As)_x + HCl.$$

o-Phenylene diarsines of the type *o*-$C_6H_4(AsMeX)_2$ are configurationally stable over a wide temperature range. The crystal structure of *o*-$C_6H_4(AsMeI)_2$ has been determined [139]. The results of the crystal structure determination verifies the original racemic structure assigned



A normal coordinate analysis of $(CH_3)_2AsH$ has been performed [140] and used to assign fundamental vibrational modes. The infra-red spectrum of $EtAsCl_2$ has been measured as a function of temperature [141]. The concentration ratio of *trans* to *gauche* conformers decreased from 1.32 to 0.38 with increasing temperature from 90-300°K.

The reaction between CH_3AsH_2 and S_2Cl_2 has been investigated [142]. At a molar ratio of 2:1, $CH_3AsH_2:S_2Cl_2$, the following stoichiometry is obeyed. However, when the molar ratio is 1:2, the $(CH_3As)_x$ initially

$$2CH_3AsH_2 + S_2Cl_2 \longrightarrow CH_3AsCl_2 + 2H_2S + 1/x(CH_3As)_x$$

formed disappears and is converted to methyldichloroarsine. At the latter molar ratio the reaction can be represented as

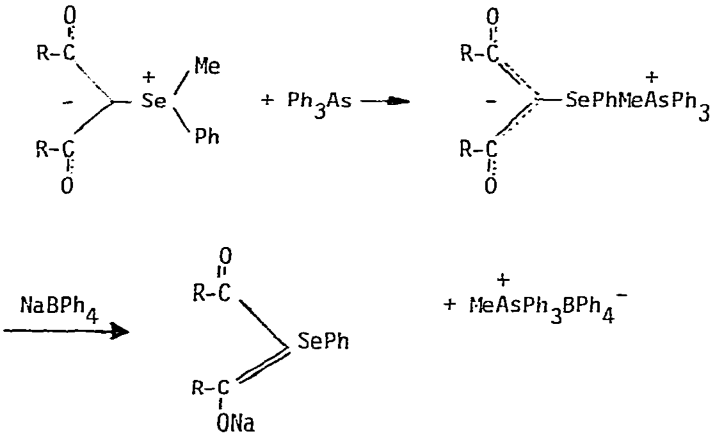
$$CH_3AsH_2 + 2S_2Cl_2 \longrightarrow CH_3AsCl_2 + 2HCl + \tfrac{1}{2}S_8$$

The ternary recombination of atomic iodine in the presence of $(CF_3)_2AsI$ was investigated by the method of flash photolysis in combination with kinetic spectroscopy [143]. Over the range of temperatures and pressures investigated the process proceeds in accordance with a third-order law. Rate constants are reported. The dipole moments of a series of compounds, $RC_6H_4AsCl_2$ (R = H, 4-Me, 4-halo, 4-NO_2, 2-Me, 2-halo, 2-NO_2, 2-MeO) have been measured [144]. In the *ortho*-substituted derivatives the plane of the benzene ring bisects the Cl-As-Cl angle.

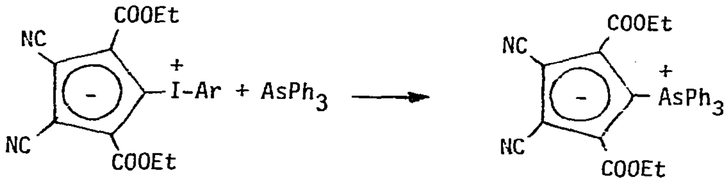
X. ARSONIUM COMPOUNDS, YLIDES, AND ARSANES

Methyl*bis*(α-naphthyl)alkylarsonium iodides are prepared by quaternization of the arsine $(naphth)_2AsR$ (R = Me, Et, Me_2CH, Bu, Me_2CHCH_2, *n*-pentyl, isopentyl) with methyl iodide [145]. With $Mg(ClO_4)_2$, the arsonium iodides exchange anions to give the perchlorates $(naphth)_2AsRMeClO_4$. The quaternization of compounds containing simultaneously both amino and arsino groups has been investigated [146]. In order to determine whether arsenic or nitrogen is quaternized, ^1H NMR was utilized as the investigative probe. This is based on the following observations: a methyl group on a quaternary arsenic gives a

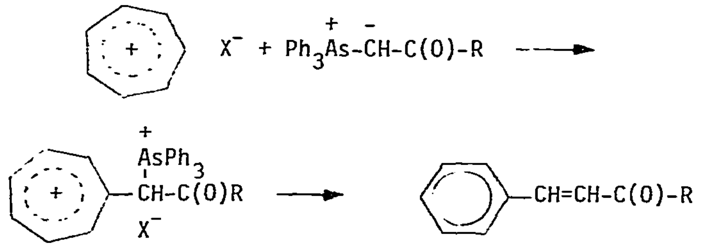
^1H NMR signal at 1.35-2.60 ppm, the signal of a methyl group on trivalent nitrogen occurs at 2.99-3.06 ppm, and methyl groups on a quaternary nitrogen are observed at 3.66-3.99 ppm. Quaternization of a series of molecules of the type $R_2RNZAsR'_2$, where Z is a bridging group such as C_6H_4 was studied. If the substituents on both the arsenic and the nitrogen are close in size and inductive effect, methyl iodide adds to the arsenic atom, as in the case of *p*- and *m*-(diethylarsino)-N,N-dimethylaniline derivatives. When bulky, or strongly electron-accepting aryl substituents are present on the arsenic atom, if two methyl groups are bonded to nitrogen, quaternization occurs at the amino group. The reaction between selenium ylides and triphenylarsine in the presence of tetraphenylborate yields arsonium tetraphenylborates [147]. The reaction is described by the following equation.



Aryliodonio-cyclopentadienides react with triphenylarsine to yield arsonio-cyclopentadienides [148]. The reaction requires a temperature of 140-150° and catalyses by Cu(I) compounds.

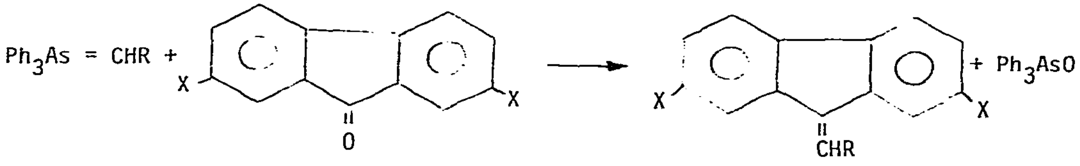


Cavicchio and co-workers [149] studied the reaction between carbonyl stabilized arsenic ylides and tropylium salts in THF at room temperature. The first step involves the formation of the tropenyl salt which can be isolated or identified spectroscopically. The salt can undergo rearrangement to the styryl compound.



Russian workers [150] have prepared $Cl_3SiN = AsPh_3$ by the reaction between $Cl_3SiN(Cl)SiMe_3$ and $AsPh_3$.

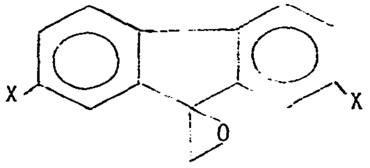
Arsonium salts and ylides have been utilized for a number of synthetic procedures. Semi-stabilized ylides undergo reaction with 2,7-dinitro and 2,7-dibromofluorenones at reflux temperature (benzene) to give exocyclic olefins exclusively [151], e.g., the 2,7-dinitro and 2,7-dibromo-9-arylidene fluorenes.



A *B* *C*

(*A*,*C*) R = $2\text{-}NO_2C_6H_4$, $3\text{-}NO_2C_6H_4$, $4\text{-}NO_2C_6H_4$, $4\text{-}IC_6H_4$
(*B*,*C*) X = Br, NO_2

The reactions of the non-stabilized ylide (A, R = H) were carried out at room temperature. This reaction afforded the epoxide, i.e., the 2,7-disubstituted fluorene-9-spirooxiranes, *D*.



D

The reaction between 4-chlorobenylidenetriphenylarsenane and aromatic aldehydes has been investigated [152]. This particular ylid carries an electron donating group. Quaternization of triphenylarsine with 4-chlorobenzyl bromide in acetone affords 4(chlorobenzyl)-triphenylarsonium bromide. The latter is converted to 4-chlorobenzylidenetriphenylarsenane (*E*). The reaction of *E* with a number of mono- and disubstituted benzaldehydes resulted in the exclusive formation of *trans*-4-chlorostilbenes. The ylide (*E*) was also found to react smoothly with 2-furfural to give *trans*-2-(4-chlorostyryl)furan. The presence of electron groups was found to enhance the yield while electron donating groups were found to decrease the yield of olefin. The authors claim that their observations prove "beyond doubt" [cf. Trippett and Walker, J. Chem. Soc., (C), 1114 (1971)] that solvent and base, apart from other structural factors, are also responsible for determining the course of reaction between semi-stabilized ylids and carbonyl compounds.

Diazo coupling to benzene is possible when the ring does not bear strongly electron-donating groups if the leaving group is phosphonium, arsonium, or stibonium [153]. The following reaction takes place between pentaphenylarsenic and a diazonium fluoborate in acetonitrile-tetrahydrofuran solvent. The reaction between phenacyltriphenylarsonium

$$(C_6H_5)_5As + 4\text{-}RC_6H_4N{\equiv}N^+BF_4^- \longrightarrow (C_6H_5)_4As^+BF_4^- + C_6H_5N{=}NC_6H_4R\text{-}4$$

bromide and aromatic primary amines furnishes a good method for the synthesis 2-arylindoles, and 2-arylbenzindoles [154]. The reaction proceeds by way of an arsenic ylide.

A ^{13}C NMR investigation of ylides has been published [155]. In this particular study, chemical shifts and one-bond coupling constants for the ylidic carbon, C(1) in keto-stabilized phosphonium, arsonium and sulfonium ylides show that C(1) has an *sp*^{2} hybridized carbanionic structure with a strong electron drift to the carbonyl. Carbonyl stabilization of the negative charge on C(1) depends on the onium group in the order: $Ph_3P^+ < Ph_3As^+ \approx Me_2S^+ << Me_2C_5H_3N^+$. When the ylides are complexed to $PdCl_2$, ^{13}C NMR shift studies confirm that the ylidic carbon is bonded to Pd and that C(1) bonded to the metal has a higher electron density than C(1) in the free ligand.

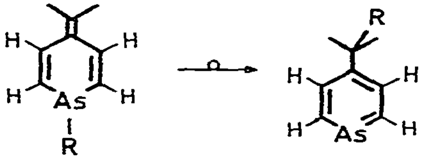
An *ab initio* LCAO-MO-SCF study of methylenearsorane, H_3AsCH_2, has been published by Strich [156]. The study shows a planar stereochemistry at the ylidic carbon atom. This result is rationalized in terms of a maximum heteroatom-carbon π-overlap. The As-C bond length in H_3AsCH_2 is 1.782 Å.

The polarized infra-red reflectivity of single crystal methyltriphenylarsonium tetracyanoquinodimethanide has been measured over the range 40-40,000 cm^{-1} [157]. The results were evaluated to obtain the dielectric function and conductivity. For E||b polarization, a very strong coupling between TCNQ intramolecular vibrations and electronic motion is observed. The bare electronic absorption is modelled by a sum of two classical oscillators. Iida [158] has studied the phase transition and thermodynamic properties of solid solutions with anion radical salts of $[(C_6H_5)_3AsCH_3]_x^{+\cdot}(TCNQ)_2^{-\cdot}$, $(0 \leq x \leq 1)$. These solid solutions are stable over a side temperature range from ≈0°K to decomposition temperatures and in the whole composition range from x = 0.00 to x = 1.00. Chesnut and Bondeson [159] have developed a model for motional correlation effects of random-walking particles with spin in one dimension. The model has been applied to proton spin-lattice relaxation in the $[(C_6H_5)_3AsMe](TCNQ)_2$ triplet exciton ion radical salt. The limitations and extensions of the model are discussed. The single ion thermodynamics of $(C_6H_5)_4As^+(C_6H_5)_4B^-$ has been the subject of two extensive studies. Abraham and Nasehzadeh [160] have calculated the free energy, enthalpy, and entropy of transfer of $(C_6H_5)_4As^+ = (C_6H_5)_4B^-$ by dividing the total transfer values into neutral and electrostatic contributions. Good agreement was obtained between calculated and observed values. A lengthy critique of the tetraphenylarsonium tetraphenylborate assumption for single ion thermodynamics in amphiprotic and dipolar-aprotic solvents has been published by Kim [161]. The results of this detailed study corroborate the $(C_6H_5)_4As(C_6H_5)_4B$ assumption which enables the determination of thermodynamic quantities for single ions, with the reservation that an asymmetric partition, with a constant partition factor for all solvents, is clearly preferred to the equal partition practiced in the literature.

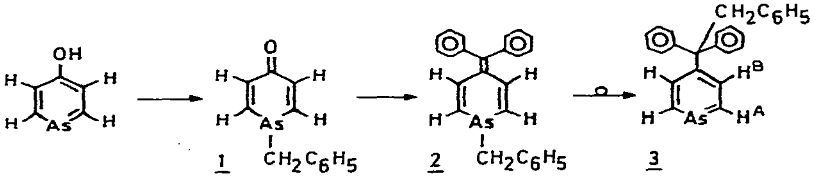
XI. ARSENIC HETEROCYCLES

An unusually large number of papers in the field of heterocyclic compounds of arsenic has been published since this review last appeared. Interest in arsabenzene, its structure and chemistry, has been especially high. The bulk of this work originates from the laboratories of A. J. Ashe in Michigan and Von G. Märkl in Regensburg. Dissertations by T. W. Smith and W-t. G. Chan are concerned with group V heterobenzenes. The key conclusion reported in the dissertation of Smith [162] is that "...the λ^5-heterobenzenes are not aromatic compounds and the six π-electrons remain localized on carbon." Smith also found that methyllithium adds to the electropositive heteroatom of the λ^3-heterobenzenes. This process disrupts the aromaticity of the system and yields an anion similar in electronic structure to the λ^5-heterobenzenes. Also, arsabenzene reacts with electrophilic reagents to give aromatic substitution products rather than addition products. Chan [163] has investigated a number of synthetic pathways to the substituted arsabenzenes. One involves the synthesis of 4-methyl stannacyclohexadiene which is then converted to the 4-methyl arsabenzene. 3-Methyl-1,4-pentadiene can be prepared by the copper-catalyzed coupling reaction between an ethynyl Grignard reagent and a secondary propargyl bromide. This leads to 4-methyl arsabenzenes. 2-Substituted arsabenzenes were prepared from the corresponding 1,4-pentadiynes. Ashe and Chan [164] have reported on the reaction of 1,4-diynes with dibutyltin hydride to give 2-alkyl-1,1-dibutyl-1,4-dihydrostannabenzenes. These react with arsenic trichloride. For example, 6-acetoxy-1,4-hexadiyne is converted to 2-arsabenzyl acetate and subsequently to a number of 2-functionalized arsabenzenes. Arsabenzene easily undergoes Friedel-Crafts acylation [165]. Acetylation of arsabenzene at -70° in methylene chloride with CH_3COCl in the presence of anhydrous aluminum chloride gave monaacetylarsabenzenes in yields up to 80%. The distribution of isomers, as determined by ^1H NMR was 80% of the 4-acetyl isomer and 20% of the 2-acetyl isomer. When the γ-position is blocked, substitution takes place at the α-position. Thus, 4-methylarsabenzene gives 50% 2-acetyl-4-methylarsabenzene.

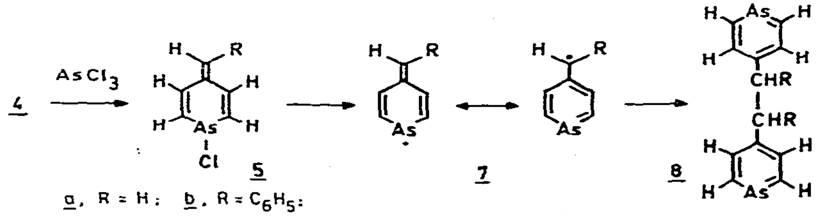
Märkl and Rampal [166] have examined the potential thermal rearrangement of 1-R-4-methylene-arsacyclohexadiene-2,5 to the arsabenzene, as shown below, Thus, at 135-140°, the reaction between 1 and



diphenylketene yielded 2 which underwent a thermal rearrangement at 150° to 3.

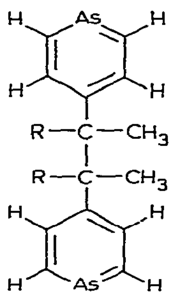


When 4-methylene-1,1-di-*n*-butyl-1-stannacyclohexadiene-2,5 (4) was treated with arsenic trichloride or an organylarsenic dichloride, reaction



a, R = H; b, R = C_6H_5:

products of the type 8, 10, 11, and 12 were obtained. Hence, free radical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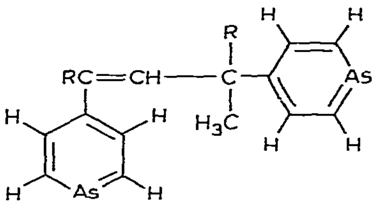
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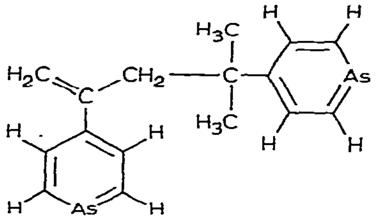
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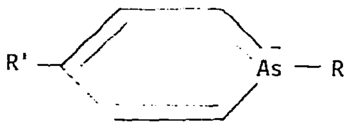
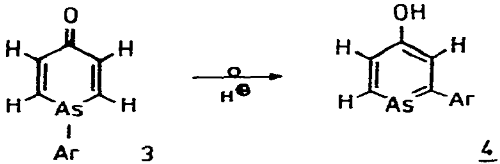
a, R=H; b, R=CH_3

intermediates, 5 and 7, are proposed. The formation of the 4-methylene-1-organylarsenacyclohexadiene-2,5 as an intermediate and its subsequent thermal rearrangement does not seem to occur.

The effect of functional groups on the reactivity of C_5H_5As has been investigated [167]. Functional groups studied included -OH, -COOH, -C(O)OR and -CHO. Substitution by an aldehyde or carboxylic acid group in the 4-position enhances the electrophilic character of the hetero atom. An alkoxy or hydroxyl group substituted in the 4-position decreases the electrophilic character of the hetero atom. If an aldehyde function is at the 4-position, it is preferentially attacked by a weak base and a Wittig-type reaction occurs at that group. Strong bases, such as LiR, attack the hetero atom to form



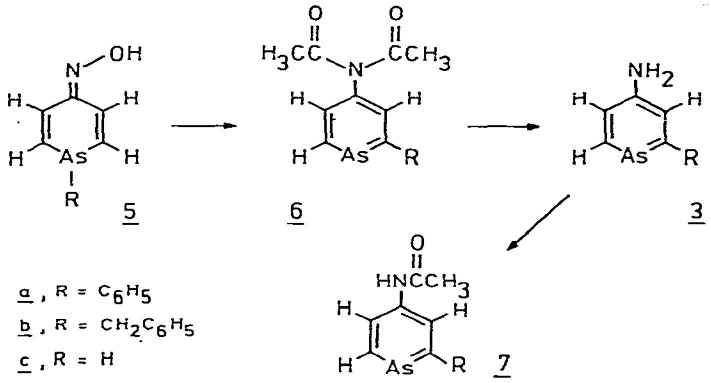
The rearrangement of an As-aryl substituted arsacyclohexadiene-4-one (3, below) to 4 has been studied [168]. The best experimental conditions



3
4

to effect this rearrangement are acetic anhydride containing catalytic concentrations of sulfuric acid at room temperature.

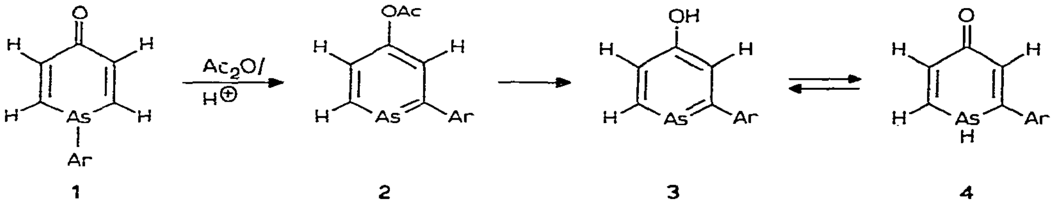
The reaction between 1-phenyl-arsacyclohexadiene-2,5-4-one and hydroxylamine hydrochloride yields the oxime (5, below). In acetic



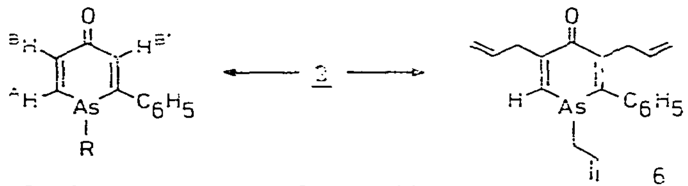
a, R = C_6H_5
b, R = $CH_2C_6H_5$
c, R = H

anhydride, 5 undergoes the expected rearrangement, but unexpectedly, the diacetamide, 6, is formed. The 4-amino derivative, 3, is formed by alkaline hydrolysis of 6. Acetylation of 3 yields only the monoacetamide which indicates that 3 is not an intermediate in the rearrangement of 5 to 6 [169].

Based on spectral observations [170], 4-hydroxy-arsabenzenes bearing a 2-aryl substituent exist entirely in the enol form (3, below). The

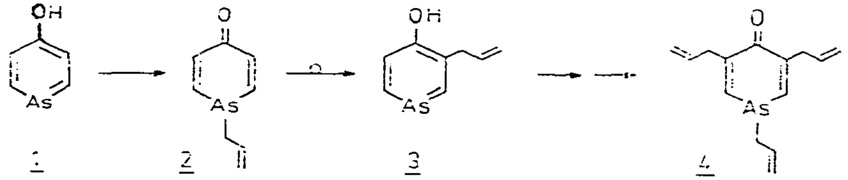


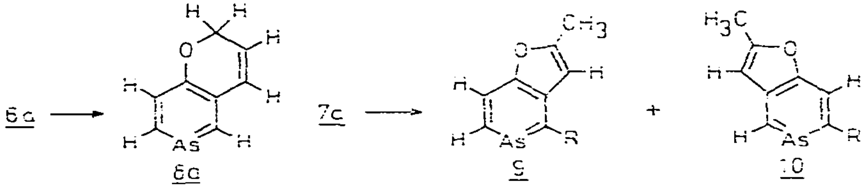
reaction of 3 with benzylbromide or the methyl ester of bromoacetic acid yields the As-substituted arsacyclohexadienone, 5. However, with allyl bromide, the 1,3,5-triallyl derivative 6 is obtained.



5a, R = $CH_2C_6H_5$; 5b, R = CH_2COOCH_3

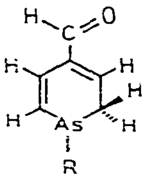
Märkl and Rampal [171] in a study closely related to that just preceding, have found that 4-hydroxyarsabenzenes, (1, below), in acetone at room temperature, do not undergo the hetero-Cope rearrangement. However, in refluxing benzene, depending upon the nature of the substituent at the 2-position, a series of ring closures take place on treatment with propargyl bromide followed by vacuum distillation. Several pyrans and furans can be obtained, several of which are shown below.





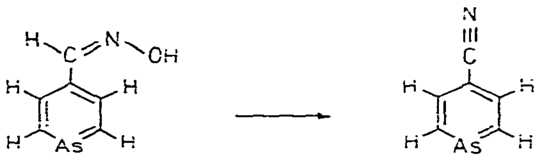
9a, 10a, R = C_6H_5; 11, R = H

The reaction of arsabenzaldehyde with C_6H_5MgBr or phenyllithium, followed by hydrolysis, gives 1-phenyl-1,2-dihydroarsabenzene-4-carbaldehyde (4a, below). When α-naphthylmagnesium bromide is used, 4b is formed [172].



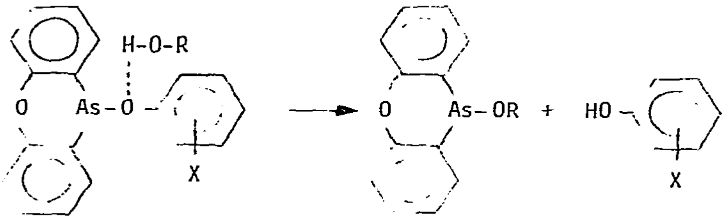
4a, R = C_6H_5
4b, R = α-Naphthyl

With malonic acid, a Knoevenagel condensation occurs. The aldehyde group also undergoes conventional reactions to form the oxime which can be converted to the arsabenzonitrile.



The ^{1}H NMR spectrum of arsabenzene partially oriented in a nematic liquid crystal [173] has been reported. The structure deduced from these studies was in excellent agreement with that previously obtained from electron diffraction and microwave measurements. An analysis of the vapor-phase structure of arsabenzene based on electron diffraction and microwave data has been detailed by Wong and Bartell [174]. The molecule was found to have a planar C_{2v} structure. Principal structural parameters and uncertainties were: r_g(C-As) = 1.850(2) Å, $r_g(C_2\text{-}C_3)$ = 1.392(9) Å, $r_g(C_3\text{-}C_4)$ = 1.4000(10) Å, r_g(C-C mean) = 1.396(2) Å, angle CAsC = 97.0(3)°, angle AsCC = 125.3(7)° and angle $C_2C_3C_4$ = 123.9(13)°. Core-ionization energies and proton affinities for arsabenzene, phosphabenzene, arsine, trimethylarsine, phosphine, and methylphosphines have been investigated [175]. The anomalously low basicities of arsabenzene and phosphabenzene are attributed to the inability of these compounds to undergo geometric rearrangement on protonation. In a study similar to that previously mentioned [174], Wong, et al. [176], have measured the ^{1}H NMR spectrum of 4-methylarsabenzene oriented in a nematic solvent. Good agreement was obtained with structural parameters obtained from electron diffraction and microwave spectroscopy.

The widespread application of phenoxarsine derivatives as additives to polymeric compositions for protection against microbial and fungicidal attack has prompted additional research concerned with this heterocycle. The kinetics of hydrolysis and alcoholysis of 10-(aryloxy)phenoxarsines has been studied as a function of the nature of the substituent in the group undergoing elimination [177]. The reactivity was found to increase with increasing electron-donor tendency of the substituent. The determining factor in the reaction mechanism involves the transfer of a proton to the oxygen atom of the As-O-C link. The following scheme is proposed.

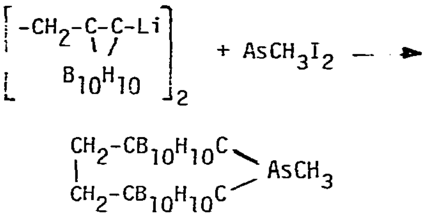


In a virtually identical study [178], a conclusion parallelling that just preceding was reached. The kinetics of the reaction between 10-phenylphenoxarsine and methyl iodide in acetone has been studied [179]. The reaction is reversible and is first order with respect to each component, or second order, overall. In a closely related study [180] the quaternization of 10-alkylphenoxarsines by methyl iodide was investigated. The rates of quaternization was found to depend primarily on the inductive effect of the substituent. In another very similar study [181], the quaternization, by methyl iodide, of five 10-arylphenoxarsines was measured. It was again found that overall effect of a *para*-substituent on the benzene ring is dependent on the induction and resonance components to about the same degree. In the case of *meta*-derivatives the resonance component exerts a greater influence.

Widespread interest in the carboranes has resulted in synthetic and physico-chemical studies of derivatives bearing a hetero atom such as arsenic. Thus, 2,3,5,6-*bis*(*o*-carborano)-4-methylarsacyclohexane [182] was prepared by the addition of methyldiiodoarsine to lithiated *bis*(*o*-carboranyl)methane,

$$H_2C(CB_{10}H_{10}CH)_2 \xrightarrow[MeAsI_2]{2n\text{-}C_4H_9Li} H_2C(CB_{10}H_{10}C)_2AsMe$$

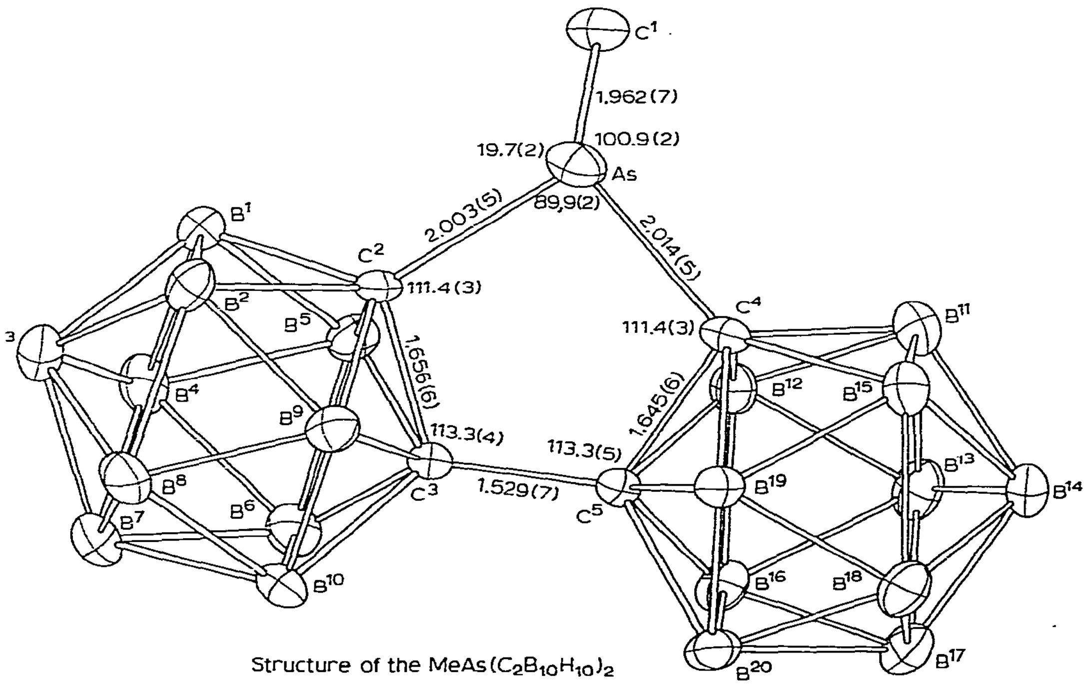
In a similar manner, seven-membered heterocycles were prepared [183] by the reaction between dilithium 1,2-*bis*(*o*-carboranyl)ethane and CH_3AsI_2



$$\left[-CH_2-\underset{B_{10}H_{10}}{C-C}-Li\right]_2 + AsCH_3I_2 \longrightarrow \begin{matrix} CH_2-CB_{10}H_{10}C \\ | \\ CH_2-CB_{10}H_{10}C \end{matrix} > AsCH_3$$

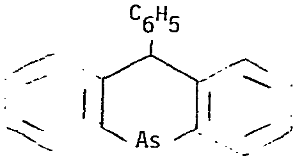
Little [184] has prepared $1,2\text{-}B_{10}H_{10}AsSb$ by the reaction between $B_{10}H_{12}As^-$ with $SbCl_3$ in the presence of triethylamine.

The crystal structure of $MeAs(C_2B_{10}H_{10})_2$ has been determined [185] and is reproduced below. In this structure, the five-membered ring containing the arsenic atom is essentially planar. The molecular structure of the *p*-arsacarborane $1,12\text{-}AsCHB_{10}H_{10}$ has been investigated by gas phase electron diffraction methods [186]. One salient feature of these measurements is that the measured B-X bond length, 2.137 Å is considerably greater than the value calculated from the sum of the single bond radii, $r_B + r_{As} = 2.00$.

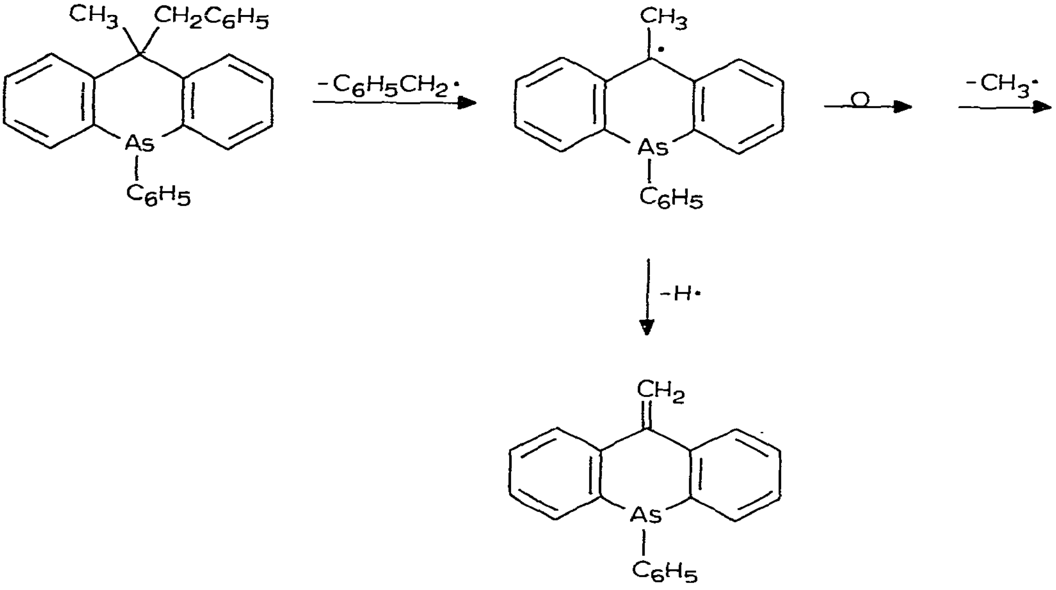


Structure of the $MeAs(C_2B_{10}H_{10})_2$

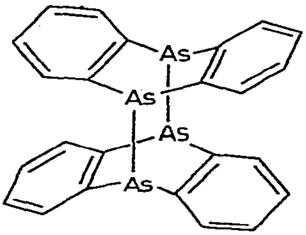
Arsaanthracenes have been the subject of several studies. The flash vacuum pyrolysis of 9-aryl-9,10-dihydro-9-arsaanthracene (below) at ∿500° yields 10-aryl-9-arsaanthracenes [187].



The yield of product depends on the nature of the substituents. The formation of free radicals as intermediates is discussed. In a related publication, Weustink and co-workers [188] discuss this free radical mechanism in greater detail. The principal pathways of their proposed mechanism is shown in the scheme below.

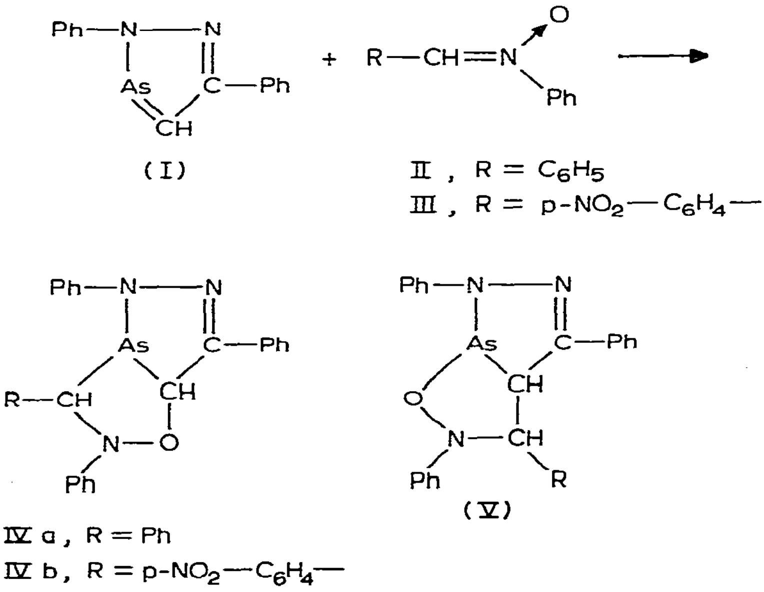


Bickelhaupt's group has prepared the first known derivative of arsanaphthalene [189]. The structure of arsanthrene has been re-investigated [190]. Based primarily on molecular weight measurements and mass fragmentation behavior, the molecule is assigned a dimeric structure having arsenic-arsenic bonds. The crystal structure of



trans-10-benzyl-9-phenyl-9,10-dihydro-9-arsaanthracene has been determined by Stam [191]. The arsaanthracene ring system is folded with an angle of 133° between the benzene rings. The crystals consist of molecules of a single type; the molecules show conformational chirality.

The cycloaddition of nitrones to the -As = C double bond has been demonstrated by Russian workers [192]. Thus, over a period of 2.5 months, C,N-diphenyl- and C-*p*-nitrophenyl-N-phenylnitrones undergo 1,3-dipolar addition to 2,5-diphenyl-1,2-diaza-3-arsene to give cycloaddition products. The reaction is illustrated below.



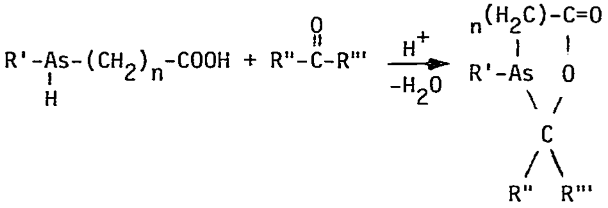
(I)

II , R = C_6H_5
III , R = p-NO_2—C_6H_4—

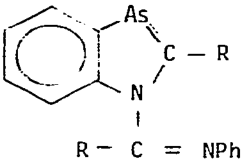
IV a , R = Ph
IV b , R = p-NO_2—C_6H_4—

(V)

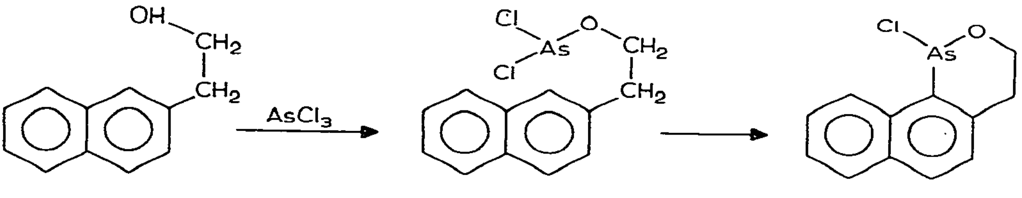
As is illustrated by the following equations, the addition of phenylarsinoacetic, β-*n*-butylarsino- and β-phenylarsinopropionic acids to aldehydes and ketones, followed by intramolecular condensation, leads to the formation of 1,3-oxarsolan-5-ones and 1,3-oxarsenan-6-ones, respectively [193]. The structures of the compounds were deduced from



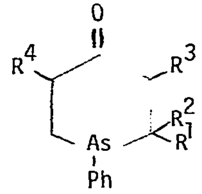
their infra-red, ^1H NMR and mass spectra. Heinicke and Tzschach [194] have synthesized 1H-1,3-benzazarsoles. This was done by the reaction between *o*-aminophenylarsine and an iminoester hydrochloride.



The isomeric 3H-1,3-benzazarsoles were synthesized from secondary *o*-aminophenylarsines and *N*-phenylimide chlorides. Spectroscopically, the 1H-1,3-benzazarsoles behave as aromatic compounds. The reaction of arsenic trichloride with 2-(β-naphthyl)ethanol followed by cyclization of the dichloride intermediate gives 1-chloro-3,4-dihydro-1H-naphth[1,2-*C*][1,2]-oxarsenic [111] [195].

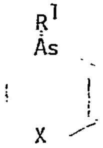


Bosyakov and co-workers [196] described the synthesis of a series of compounds having the ring system illustrated.



R_1-R_3 = H, Me; R^4 = OH, NH_2

Maerkl, Baier and Liebl [197] have investigated the heterocyclic ring systems (shown below) formed by the cycloaddition of diynes, HC≡CXC≡H with R^1AsH_2.

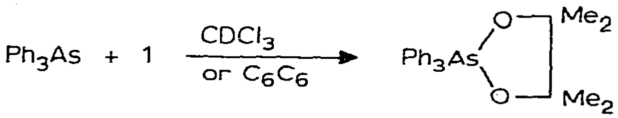


R_1 = Ph, *p*-tolyl, *p*-$(Me_2N)C_6H_4$

X = CR(OMe) R = Ph, Me, Me_3C, cyclohexyl, 1-naphthyl, *p*-anisyl;

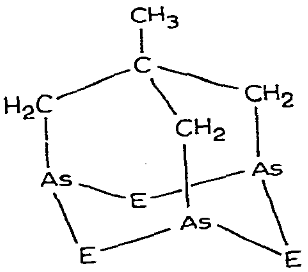
X = $PCMe_3$, $SiMe_2$, $SiPh_2$

The reaction of triphenylarsine with tetramethyl-1,2-dioxetane (1) produces 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane [198].

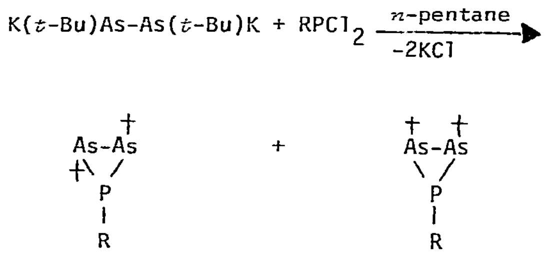


The observed relative reactivities are $Ph_3P \geq Ph_3Sb > Ph_3As$. The greater reactivity of Ph_3Sb relative to Ph_3As may be attributable to greater availability of *d* orbitals in antimony requisite for bonding with the peroxide.

The crystal structure of the heteroadamantane shown below, where E is sulfur, has been determined by Ellermann and co-workers [199]. The unit



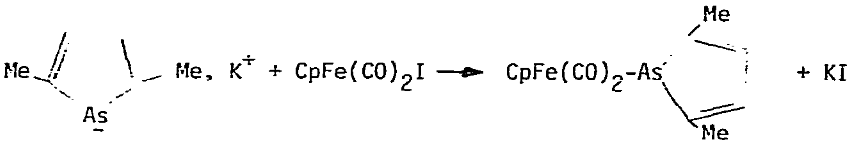
cell (space group $P2_1/n$) contains four molecules in cubic closest packing. The molecule possesses an enlarged cage structure with a large C-CH_2-As bond angle of 124°. The compound is synthesized in good yield by the reaction of 1,1,1-*tris*(diiodoarsinomethyl)ethane, $H_3CC(CH_2AsI_2)_3$ with H_2S in tetrahydrofuran. McKerley, et al. [200], have prepared the oxygen analogue of the adamantane just described [199]. This was done by using water in place of H_2S. The crystal structure was also determined and following are the salient features: As-As, average distance = 3.165 Å; average As-O, As-C, and C-C distances are, respectively, 1.77, 1.96, and 1.53 Å. The average values of the O-As-O and O-As-C angles are 100.5 and 97.7°. The reaction between Rb_3As_7 and $ClSiMe_3$ gives 4,7,11-*tris*(trimethylsilyl)tricyclo[2.2.1.$0^{2,6}$]heptaarsane, $As_7(SiMe_3)_3$. Crystal data on this compound have been obtained [201]. Baudler and Habermann [202], by the use of low temperatures and non-polar solvents, have prepared some phosphadiarsirane. The reaction is summarized below.



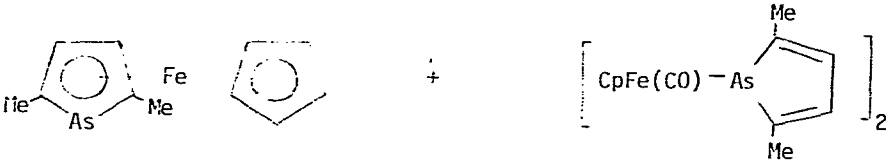
a *b*

At -78°, if R = ethyl, oligomerization occurs. However, if R = isopropyl, isomer *a* can be obtained and fully characterized, even if the reaction is carried out at 0°. Other heterocyclic derivatives of the following types are also formed during this reaction: $(t\text{-BuAs})_3PR$, $(t\text{-BuAs})_2(PR)_2$, $[(t\text{-BuAs})\text{-}(PR)]_2$ and $t\text{-BuAs}(PR)_3$.

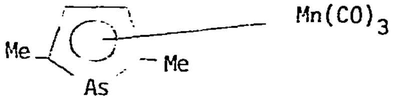
A red, σ-bonded Fe-As complex has been described by Thiollet and co-workers [202a]. It is formed by the reaction between 2,5-dimethylarsolylpotassium and cyclopentadienyl dicarbonyl iron iodide:



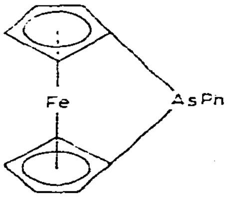
When the σ-bonded complex is decomposed in boiling xylene, it yields two new arsolyl complexes:



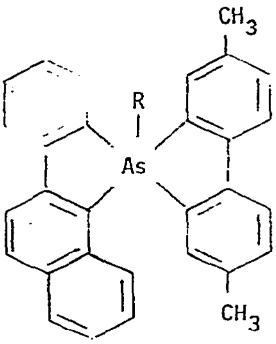
The dimeric σ-complex is a mixture of 90% "*cis*" and 10% "*trans*" isomers. The arsolyls act as three-electron bridging ligands through their arsenic atoms. The "*cis*" and "*trans*" isomers were identified by the use of ^1H NMR spectroscopy, in particular, with respect to the equivalence or non-equivalence of the substituent methyl groups. The same group [203] has reported the synthesis of 2,5-dimethylarsacymantrene by the reaction of 1-phenyl-2,5-dimethylarsole with $Mn_2(CO)_{10}$ in boiling xylene. This compound undergoes reaction with acetyl chloride in the presence of aluminum chloride to form the 3-acetyl derivative. Seyferth and Withers [204] have prepared (1,1'-ferrocenediyl)-phenylarsine (below). This compound is formed by the reaction of 1,1'-dilithioferrocenetetramethylenediamine with $PhAsCl_2$.



2,5-dimethylarsacymantrene (yellow)

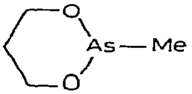
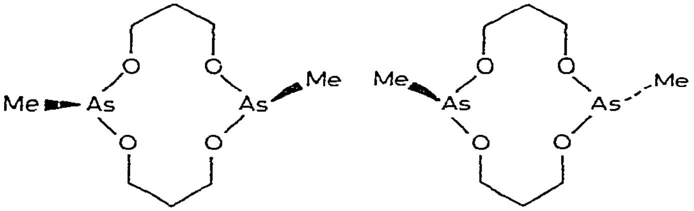
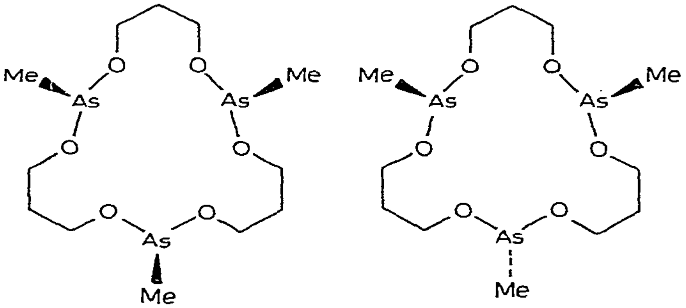


Hellwinkel and co-workers [205] have carried out a ^1H NMR investigation of some overcrowded asymmetric phosphoranes, arsoranes and stiboranes. The actual biarylylenearsorane studied is shown below, where R = phenyl or biphenylyl. The two different methyl positions are

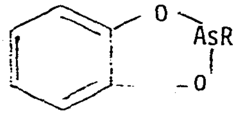


reversibly equilibrated at elevated temperatures. The free enthalpies of activation were measured. An interpretation is offered starting with a trigonal bipyramidal ground state conformation. The ligand exchange phenomena are interpreted in terms of a pseudorotation process and trigonal, bipyramidal transition states with diequatorial biarylylene groups.

Both ^1H and ^{13}C NMR analyses have been utilized in conformational studies of 1,3-dioxa-2-arsacyclohexanes. Aksnes and co-workers [206] have carefully analyzed the ^1H NMR spectra of 22 1,3,2-dioxaarsenanes. These molecules have a chair conformation with the substituent on arsenic oriented axially. When the ring substituents are methyl, *t*-butyl, or phenyl, they are equatorially oriented unless they are forced into axial positions by *gem*-disubstitution forces. The O-C-C-C-O portion of the six-membered ring assumes a staggered configuration. Ring protons oriented in the axial position are shifted downfield relative to the equatorially oriented protons. Alkyl and phenyl ring-substituents affect both the chemical shifts and coupling constants of the ring protons. Thus, an equatorial methyl group produces a significant chemical shift of -0.2 to -0.5 ppm on the *vic*-axial proton. When an equatorial substituent is introduced on one of the carbon atoms bearing the coupled protons the *vic*-coupling constant is reduced by 1 Hz, or more. The oxygen hetero atom causes an increase of about 3 Hz in the *gem*-coupling constant of adjacent methylene protons with respect to carbon. Cazaux, et al. [207] have observed, from ^1H and ^{13}C NMR data, the existence of dimers and trimers in solutions of 2-methyl-1,3-dioxa-2-arsacyclohexanes. The structures of the monomer and associated forms reported by these workers are given in the table just below.

Substances	Isomers	No. of Me - As signals
 (1)	1	1
 (2)	2	1 + 1
 (3)	2	1 + 1 + 1

Anchisi and co-investigators [208] have synthesized benzodioxole derivatives as shown below, by heating the analogue containing $SnMe_2$ at



the hetero atom position with $Cl_2AsR{\cdot}Me_2SnCl_2$ sublimes leaving the arsenic heterocycle.

XII. BIOCHEMICAL AND ENVIRONMENTAL ASPECTS OF ARSENIC COMPOUNDS

The phospholipid, *O*-phosphatidyltrimethylarsonium lactic acid has been isolated from marine algae cultured in ^{74}As-arsenate [209]. The biological transformation of arsenate by marine algae leads to the accumulation of the arsoniumphospholipid as a major reservoir for arsenic. In food chains, it can be degraded to trimethylarsonium betaine, dimethylarsinic acid methylarsonic acid or arsenate.

"Interactions Between Arsenic Species and Marine Algae" is the title of a doctoral dissertation by Grady [210]. Arsenic concentrations among different marine algae were found to vary from 0.4 to 23 ng mg^{-1}. The Phacophyceae were found to contain more arsenic than other algal classes and a greater proportion of organic arsenic. Among macroalgae the inorganic arsenic concentrations were found to be fairly constant. Although phytoplankton take up As(V) readily, the majority is released to the media in reduced and methylated forms. Up to half the arsenic may be reduced. Arsenate competes with phosphate for up-take by algal cells. The inhibition of phosphate up-take is competitive. However, when the phosphate concentration is raised to >0.3 μM the inhibition by arsenate is relieved. As(V) stress causes the cells' phosphorus requirement to increase.

Arsenite is toxic to phytoplankton, but dimethylarsinic acid at levels of 25 μg l^{-1} did not affect cell productivity. Algae may be of major importance in converting inorganic arsenic to relatively non-toxic organic forms.

Antonio et al., have studied the methylation of arsenic species by $(CH_3)_3S^+PF_6^-$. This molecule was chosen in order to mimic more closely the *in vivo* reaction which is believed to involve the transfer of an S-methyl group and because of the weak nucleophilicity of the PF_6^- anion. Methylation of arsenate, methylarsonate and dimethylarsinate occurs at high pH [211] and higher temperatures (80°). Rate studies could not be explained in terms of the anticipated bimolecular pathway. Two other qualitative observations were reported. $[(CH_3)_2\overset{+}{S}CH_2CH_2CH(NH_2)COOH]PF_6^-$ does partially transfer its methyl group to $CH_3AsO_2^-$ at pH 5.8, but $(CH_3)_2\overset{+}{S}CH_2CH_2SO_3^-$ is inactive under these conditions. In studies related to the biological methylation of arsenic compounds, Cullen and co-investigators [212] have synthesized a number of arsinocobalooximes and determined the crystal structure of $[(CH_3)(C_6H_5)As(O)Co(III)(dmg\ H)(dmg)_2]Co(II)$. In this formula, dmg is dimethylglyoxime.

The application of high pressure liquid chromatography (HPLC) coupled to a graphite furnace as a means of separating and identifying naturally occurring organoarsenic compounds has been discussed by Zingaro [213]. Details of this analytical method which utilizes a graphite furnace, and Zeeman atomic absorption spectrometer as an automated element-specific detector for HPLC has been described by Stockton and Irgolic [214]. The use of this system furnishes a means of separation of arsenobetaine, arsenocholine, arsenite and arsenate.

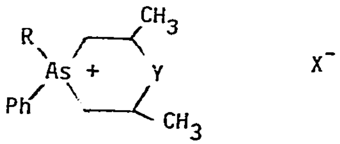
XIII. INDUSTRIAL APPLICATIONS AND MISCELLANEOUS

1-4-Heteroarsenanium salts have been reported to function as phase-transfer catalysts in the Finkelstein and Kolbe reactions [215]. These reactions are described essentially as follows:

$$RBr_{org.} + KI_{aq.} \rightleftharpoons RI_{org.} + KBr_{aq.}$$

$$RBr_{org.} + KCN_{aq.} \rightleftharpoons RCN_{org.} + KBr_{aq}.$$

The types of arsenanium salts used have the following structure:

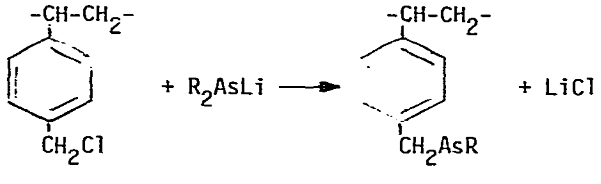


R = Ph, Me, $CH_2 = CH\text{-}CH_2\text{-}$, $PhCH_2$; Y = O, NCH_3; X^- = Br, ClO_4.

Methyl groups bound to arsenic were found to greatly reduce the catalytic reactivity of the onium salts. Alkali metal salts of R_2AsH or $RAsH_2$, where R is an aromatic or cycloaliphatic group function as polymerization catalysts for the manufacture of colorless diene polymers [216]. A patent issued to Ross [217] describes the conversion of MH_n to MR_n where M is Si, Ge, Sn, Pb, P, As, Sb or Bi by the reaction of the metal hydride to the olefin. The preparation of a number of metal alkyls in this manner is claimed. Smith [218] has been awarded a patent which describes the treatment of halomethylated polystyrenes with $ClAsPh_2$. Oxidation of the reaction products gives polystyrenes having $As(O)Ph_2$ groups attached to the benzene rings. These compounds function as catalysts for the conversion of isocyanates to carbodiimides. A very similar patent has been awarded to Alberino and Smith [219]. This patent describes the use of a polystyrene containing $As(O)Ph_2$ or $CH_2As(O)Ph_2$ groups for the conversion of $[4\text{-}(OCN)C_6H_4]_2CH_2$ to a carbodiimide containing reaction product which is stable after removal of the As-containing catalyst by filtration.

Russian workers [220] have described the synthesis of polymers containing arsines as functional groups. These polymers function as ion exchangers in a manner analogous to quaternary ammonium bases. The manner of synthesis and the type of polymers formed is shown by the following:

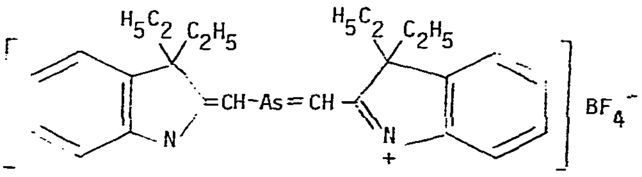
$$R_2AsBr + 2\ Li \longrightarrow R_2AsLi + LiBr$$



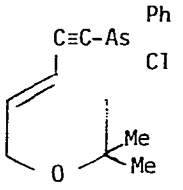
Zhukova, et al. [221] have studied porous styrene-divinylbenzene copolymers impregnated with *tris*(octyl)arsine oxide as sorbents. A method for the recovery of arsonic acids, $RAs(O)(OH)_2$ is the subject of a Japanese patent [222]. Waste liquids containing arsonic acids up to 4000 ppm are treated, following adjustment of the pH to 4.9, with zinc chloride, and the arsonic acid concentration is lowered to 100 ppm. A method for the production of the ferric salt of methanearsonic acid containing only 0.04% inorganic arsenic is described [223]. Following the conventional industrial synthesis of methanearsonate (As_2O_3 + NaOH + MeCl, pressure), the disodium methanearsonate is stirred with slaked lime, clarified, and treated with ferric sulfate. This gives the pure ferric salt.

The deposition of thin films of III-V semiconductors by the thermal decomposition of vapors of a III-V addition compound has been reported [224]. As an example, gallium arsenide layers were deposited on a number of substrates by the thermal decomposition, at 600°, of $Et_3As \cdot GaEt_2Cl$ in helium carrier gas. The substrates were a cleaved fluoride, a polished corundum, gallium arsenide and germanium. The thickness of the layers was about three microns. Rheingold and Lewis [225] have prepared a review of their work on semiconducting organoarsenic materials. The syntheses and electrical properties of polymers having the stoichiometry $(RAs)_n$ is presented.

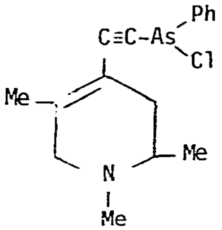
The reaction between eneamines and arsenic tribromide yields molecules suitable as dyes [226]. These have the following structure:



The nitronium ion oxidizes triphenylarsine to triphenylarsine oxide [227]. Heterocyclic acetylenic derivatives containing arsenic on the acetylenic substituent have been described [228]. They have the following structures:



or



REFERENCES

[1] R. A. Zingaro and K. J. Irgolic, J. Organometal. Chem., 138, 229 (1977).

[2] R. A. Zingaro and K. J. Irgolic, J. Organometal. Chem., 176, 245 (1979).

[3] A. Tzschach, "Arsenheterocyclen," Deutscher Verlag für Grundstoffindustrie, VEB: Leipzig, E. Ger. (1978), 233 pp.

[4] R. E. Atkinson, Rodd's Chem. Carbon Compd., (2nd Ed.), 4G, 83 (1978).

[5] R. P. Arshinova, Stroeniya i Reaktsion. Sposobnost Organ. Soedinenii, 66 (1978).

[6] A. J. Ashe, Acc. Chem. Res., 11, 153 (1978).

[7] S. S. Sandhu, M. Arshad, S. Baweja and S. S. Parmar, J. Chem. Sci., 4, 76 (1978).

[8] A. Tzschach and W. Voigtländer, Z. Chem., 19 393 (1979).

[9] S. Samaan, Methodische der Organischen Chemie (Houben-Weyl), 13, Pt. 8, 703 (1978).

[10] B. D. Chernokal'skii, V. I. Gavrilov and A. S. Gel'fond, Stroeniya i Reaktsion. Sposobnost Organ. Soedinenii, 186 (1978).

[11] Yu. F. Gatilov and V. A. Perov, Khim. Elementoorg. Soedin., 6, 14 (1978).

[12] F. D. Yambushev and V. I. Savin, Uspekhi Khimii, 48, 1093 (1979).

[13] L. C. Duncan, Annu. Rep. Inorg. Gen. Synth., 5, 111 (1977).

[14] G. O. Doak, G. G. Long and L. D. Freedman, Kirk-Othmer Encycl. Chem. Technol., 3rd Ed., 3, 251 (1978).

[15] F. Challenger, Amer. Chem. Soc. Symp. Ser., 82, 1 (1978).

[16] R. K. Bansal and S. K. Sharma, Rasayan Samiksha, 4, 1 (1977).

[17] R. G. Kostyanovskii, I. I. Chervin, K. S. Zakharov and Yu. I. El'natanov, Mendeleevsk. S'ezd Obschch. Prikl. Khim., 11th, 3, 189 (1975).

[18] P. Jutzi and M. Kuhn, J. Organometal. Chem., 174, 57 (1979).

[19] A. Tzschach, H. Matschiner and H. Biering, Z. anorg. allg. Chem., 436, 60 (1977).

[20] Yu. M. Kargin, E. V. Nikitin, O. V. Parakin, A. A. Kazakova, Yu. G. Galyametdinov and B. D. Chernokal'skii, Dokl. Akad. Nauk SSSR, 240, 1383 (1978).

[21] J. E. Lewis and A. L. Rheingold, U. S. NTIS, AD Rep. 1978, AD-A049226, 26 pp.

[22] N. Tyutyulkov, I. Petkov and P. Schuster, Phys. Status Solidi B, 86, 385 (1978).

[23] N. Tyutyulkov, Izv. Khim., 10, 523 (1977).

[24] R. D. Gigauri, L. I. Goderdzishvili, B. D. Chernokal'skii and T. N. Shatakishvili, Soobshch. Akad. Nauk Gruz. SSR, 96, 589 (1979).

[25] K. I. Kuz'min, V. G. Emelina, L. A. Pavlov and M. N. Kuz'mina, Tezisy Dokl. - Vses. Konf. Khim. Atsetilena, 5th, 231 (1975).

[26] R. D. Gigauri, B. D. Chernokal'skii, E. S. Vachnadze, L. I. Goderdzishvili and N. G. Natenadze, Soobshch. Akad. Nauk Gruz. SSR, 95, 329 (1979).

[27] A. D. Calhoun, W. J. Kobos, T. A. Nile and C. A. Smith, J. Organometal. Chem., 170, 175 (1979).

[28] N. K. Roberts and S. B. Wild, J. Chem. Soc., Dalton Trans., 12, 2015 (1979).

[29] B. A. Murrer, J. M. Brown, P. A. Chaloner, P. N. Nicholson and D. Parker, Synthesis, 350 (1979).

[30] T. Kauffmann, K-J. Echsler, A. Hamsen, R. Kriegesmann, F. Steinseifer and A. Vahrenhorst, Tetrahedron Lett., 4391 (1978).

[31] D. Herrmann and H. Scheel, Z. anorg. allg. Chem., 442, 119 (1978).

[32] H. G. Ang and W. S. Lien, J. Fluorine Chem., 11, 419 (1978).

[33] Yu. V. Belin, N. A. Polezhaeva and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 2171 (1977).

[34] R. C. Tewari and S. C. Chaturvedi, Synthesis, 616 (1978).

[35] J. I. Shulman, J. Org. Chem., 42, 3970 (1977).

[36] F. D. Yambushev, R. R. Shagidullin, S. S. Molodtsov, F. G. Khalitov, N. A. Tumasheve and N. Kh. Tenisheva, Zh. Obshch. Khim., 48, 1762 (1978).

[37] J. Mendel and A. Kolbe, Phosphorus and Sulfur, 3, 21 (1977).

[38] R. Demuth, J. Apel and J. Grobe, Spectrochim. Acta, 34A, 357 (1978).

[39] R. Demuth, J. Apel and J. Grobe, Spectrochim. Acta, 34A, 361 (1978).

[40] C. Crocker and P. L. Goggin, J. Chem. Soc., Dalton Trans., 388 (1978).

[41] A. P. Kurbakova, L. A. Leites, S. S. Bukalov, V. T. Aleksanyan and E. N. Zorina, Zh. Strukt. Khim., 19, 86 (1978).

[42] G. Davidson and S. Phillips, *Spectrochim. Acta*, *35A*, 83 (1979).

[43] G. P. Van der Kelen, M. F. Guns, L. F. Wuyts and E. Vincent, *J. Mol. Struct.*, *43*, 221 (1978).

[44] C. A. Wilkie, *J. Am. Chem. Soc.*, *100*, 2288 (1978).

[45] T. Schaefer, W. Danchura and W. Niemczura, *Can. J. Chem.*, *56*, 2229 (1978).

[46] A. K. Baev, V. V. Zharov, Yu. L. Gubar, B. G. Gribov, I. L. Gaidym and B. I. Kozyrkin, *Vses. Konf. Kalorim.*, [*Rassir. Tezisy Dokl.*], *7th*, *2*, 307 (1977).

[47] S. G. Smirnov, A. N. Rodionov, G. A. Val'kova and D. N. Shigorin, *Zh. Fiz. Khim.*, *53*, 2349 (1979).

[48] W. T. Cook, *Diss. Abstr. Int. B.*, *39*, 1303 (1978).

[49] E. B. Sokolov, B. K. Skachkov, E. A. Efremov, B. I. Kozyrkin, A. P. Ferapontov and V. A. Fedorov, *Zh. Fiz. Khim.*, *52*, 798 (1978).

[50] P. J. Busse, C-P. Hrung, K. J. Irgolic, D. H. O'Brien and F. L. Kolar, *J. Organometal. Chem.*, *185*, 1 (1980).

[51] K. Kellner, B. Seidel and A. Tzschach, *J. Organometal. Chem.*, *149*, 167 (1978).

[52] K. Issleib, A. Balszuweit and P. Thorausch, *Z. anorg. allg. Chem.*, *437*, 5 (1977).

[53] J. Heinicke and A. Tzschach, *Z. Chem.*, *18*, 452 (1979).

[54] M. Arthurs, S. M. Nelson and B. J. Walker, *Tetrahedron Lett.*, 1153 (1978).

[55] H. M. Colquhon, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Res.* (*S*), 248 (1979).

[56] V. I. Bregadze, V. Ts. Kampel and N. N. Godovikov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1951 (1978).

[57] V. I. Bregadze, V. Ts. Kampel and N. N. Godovikov, *J. Organometal. Chem.*, *157*, C1 (1978).

[58] L. I. Zakharkin and I. V. Pisareva, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1226 (1978).

[59] B. Walther and S. Bauer, *J. Organometal. Chem.*, *142*, 177 (1977).

[60] J. Heinicke and A. Tzschach, *J. Organometal. Chem.*, *166*, 175 (1979).

[61] W.-W. Du Mont, *Inorg. Chim. Acta*, *29*, L195 (1978).

[62] H. C. Nelson, *J. Chem. Ed.*, *54*, 718 (1977).

[63] A. H. Cowley, *Homoat. Rings, Chains Macromol., Main Group Elem.*, A. L. Rheingold, Ed. Elsevier, 59 (1977).

[64] D. Seyferth and J. S. Merola, *J. Am. Chem. Soc.*, *100*, 6783 (1978).

[65] E. Röttinger and H. Vahrenkamp, *Angew. Chem.*, *90*, 294 (1978).

[66] L. B. Ionov, A. P. Korovyakov and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 2396 (1979).

[67] C. R. Connell, Diss. Abstr. Int. B., 39, 766 (1978).

[68] J. Mueller, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 34B, 531 (1979).

[69] W. Wolfsberger and H. Försterling, Chem. Ber., 111, 958 (1978).

[70] C. E. Carraher, W. G. Moon and T. A. Langworthy, Amer. Chem. Soc., Div. Polym. Chem., Polymer Preprints, 17, 1 (1976).

[71] J. Dahlmann and K. Winsel, J. Prakt. Chem., 321, 370 (1979).

[72] F. Ando, J. Koketsu and Y. Ishii, Bull. Chem. Soc. Jpn., 51, 1481 (1978).

[73] J. Koketsu, H. Hayakawa, K. Kitaura, F. Ando and Y. Ishii, Nippon Kagaku Kaishi, 912 (1978).

[74] T. C. Klebach, H. van Dongen and F. Bickelhaupt, Angew. Chem., 91, 423 (1979).

[75] N. W. Alcock, E. M. Holt, J. Kuyper, J. J. Mayerle and G. B. Street, Inorg. Chem., 18, 2235 (1979).

[76] L. M. Epshtein, A. N. Zhdanova, N. S. Dolgopyat, D. A. Bochvar, N. P. Gambaryan and L. A. Kazitsyna, Izv. Akad. Nauk SSSR, Ser. Khim., 2487 (1979).

[77] R. D. Gigauri, B. D. Chernokal'skii, M. A. Indzhiya, L. I. Goderdzishvili and E. E. Gvilava, Zh. Obshch. Khim., 48, 1080 (1978).

[78] B. E. Abalonin, Yu. F. Gatilov, Z. M. Izmailova, V. I. Kukushkina, L. Lokhot-skaya and L. Denisova, Zh. Obshch. Khim., 48, 409 (1978).

[79] V. A. Valiullina and B. D. Chernokal'skii, Zh. Obshch. Khim., 48, 1083 (1978).

[80] V. A. Valiullina, B. D. Chernokal'skii and T. A. Shesternina, Zh. Obshch. Khim., 49, 1916 (1979).

[81] L. B. Ionov, A. P. Korovyakov and B. D. Chernokal'skii, Zh. Obshch. Khim., 48, 940 (1978).

[82] F. D. Yambushev, Z. I. Usmanov, R. R. Shagidullin, F. G. Khalitov, A. M. Galeev and N. Kh. Tenisheva, Zh. Obshch. Khim., 48, 1766 (1978).

[83] V. S. Gamayurova, V. K. Gordeev and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 817 (1979).

[84] R. D. Gigauri, B. D. Chernokal'skii, L. I. Goderdzishvili and T. N. Shatakishvili, Soobshch. Akad. Nauk Gruz. SSR, 88, 601 (1977).

[85] V. S. Gamayurova, V. I. Savdur and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 174 (1979).

[86] J. Slouka, Acta Univ. Palacki. Olomuc., Fac. Rerum Nat., 53, 197 (1977).
a. V. S. Gamayurova, V. K. Kuz'min, I. D. Kats and B. D. Chernokal'skii, Zh. Obshch. Khim., 48, 1575 (1978).

[87] T. Mallon and M. Wilber, Z. anorg. allg. Chem., 454, 31 (1979).
a. A. J. Dale and P. Frøyen, Acta Chem. Scand., B 31, 599 (1977).

[88] H. Wunderlich, Acta Cryst., B34, 1000 (1978).

[89] F. T. Henry and T. M. Thorpe, J. Chromatogr., 166, 577 (1978).

[90] V. Vancova, M. Melnik, G. Ondrejovic and J. Gazo, Z. anorg. allg. Chem., 455, 93 (1979).

[91] D. Cunningham, P. J. D. Hennelly and T. Deeney, Inorg. Chim. Acta, 37, 95 (1979).

[92] S. S. Sandhu, B. S. Manhas and H. S. Kohli, J. Indian Chem. Soc., 55, 328 (1978).

[93] P. G. Harrison, M. I. Khalil and N. Logan, Inorg. Chim. Acta, 30, 165 (1978).

[94] G. K. Sandhu, Indian J. Chem., Sect. A, 16A, 1105 (1978).

[95] L. M. Rajkovic-Blazer, Diss. Abstr. Int. B., 39, 3844 (1979).

[96] M. J. Kaus, Diss. Abstr. Int. B., 38, 5927 (1978).

[97] V. V. Yakshin, N. A. Lyubosvetova, M. I. Tymonyuk and B. N. Laskorin, Dokl. Akad. Nauk SSSR, 245, 1406 (1979).

[98] L. Cazaux, J-P. Gorrichon, P. Maroni and J-G. Wolf, J. Chem. Res. (S), 182 (1979).

[99] M. Geoffroy and A. Llinares, Helv. Chim. Acta, 62, 1605 (1979).

[100] J. A. Howard and J. C. Tait, Can. J. Chem., 56, 2163 (1978).

[101] V. V. Yakshin, N. A. Lyubosvetova, A. I. Zarubin and B. N. Laskorin, Zh. Fiz. Khim., 52, 1556 (1978).

[102] M. Grundwald, M. Szafron and J. Rychlewski, Pol. J. Chem., 53, 829 (1979).

[103] A. M. Rozen, Z. I. Nikolotova, N. A. Kartasheva and L. A. Kasumova, Zh. Neorg. Khim., 23, 113 (1978).

[104] B. N. Laskorin, V. V. Yakshin, E. A. Filippov and N. A. Lyubosvetova, Tezisy Dokl. - Vses. Konf. Ekstr., 3, 99 (1977).

[105] B. N. Laskorin, V. V. Yakshin, N. A. Lyubosvetova and R. G. Miftakhova, Radiokhimiya, 19, 769 (1977).

[106] R. Bravo and J-P. Laurent, C.R. Acad. Sc. Paris, Ser. C, 286, 143 (1978).

[107] J. H. Lowry, R. B. Smart and K. H. Mancy, Anal. Lett., 10, 979 (1977).

[108] B. E. Abalonin, I. I. Kosolapova, L. A. Lokhot-skaya and Z. M. Izmailova, Zh. Obshch. Khim., 49, 379 (1979).

[109] J. R. Daniel, Diss. Abstr. Int. B., 38, 1704 (1977).

[110] M. G. V. Rosenthal, Diss. Abstr. Int. B., 39, 4899 (1979).

[111] J. R. Daniel and R. A. Zingaro, Carbohydr. Res., 64, 69 (1978).

[112] C. H. Banks, J. R. Daniel and R. A. Zingaro, J. Med. Chem., 22, 572 (1979).

[113] L. B. Ionov, A. P. Korovyakov and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 2514 (1979).

[114] B. E. Abalonin, Yu. F. Gatilov and G. I. Vasilenko, Zh. Obshch. Khim., 48, 413 (1978).

[115] Yu. F. Gatilov, V. A. Perov and B. G. Zateev. Zh. Obshch. Khim., 48, 1771 (1978).

[116] V. Krishnan, A. Datta and S. V. L. Narayana, Inorg. Nucl. Chem. Lett., 13, 517 (1977).

[117] Yu. F. Gatilov, V. A. Perov and B. G. Zateev, Zh. Obshch. Khim., 48, 1840 (1978).

[118] A. Andrä and K. Andrä, Z. anorg. allg. Chem., 434, 127 (1977).

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

[120] A. Darmadi, A. Haas and M. Kaschani-Motlagh, Z. anorg. allg. Chem., 448, 35 (1979).

[121] P. M. Boorman, P. W. Codding and K. A. Kerr, J. Chem. Soc., Dalton Trans., 1482 (1979).

[122] V. E. Zavodnik, V. K. Bel'skii and I. P. Gol'dshtein, Zh. Strukt. Khim., 20, 152 (1979).

[123] G. Beurskens, P. T. Beurskens, J. H. Noordik, J. Willemse and J. A. Cras, Recl. Trav. Chim. Pays-Bas, 98, 416 (1979).

[124] D. J. Williams, C. D. Quicksall and K. J. Wynne, Inorg. Chem., 17, 2071 (1978).

[125] D. J. Williams and K. J. Wynne, Inorg. Chem., 17, 1108 (1978).

[126] R. R. Shagidullin, S. V. Izosimova and D. F. Fazliev, Izv. Akad. Nauk SSSR, Ser. Khim., 350 (1978).

[127] V. M. Tsentovskii, I. B. Ryabchenko, V. S. Tsentovskaya and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 1812 (1979).

[128] D. U. Zakirov, Yu. G. Galyametdinov, B. D. Chernokal'skii and I. A. Safin, Zh. Fiz. Khim., 53, 133 (1979).

[129] R. D. Gigauri, Z. L. Tigishvili, B. D. Chernokal'skii and L. I. Goderdzishvili, Zh. Obshch. Khim., 47, 2226 (1977).

[130] R. D. Gigauri, B. D. Chernokal'skii, L. I. Goderdzishvili and T. N. Shatakishvili, Zh. Obshch. Khim., 49, 181 (1979).

[131] A. Otero and P. Royo, J. Organometal. Chem., 171, 333 (1979).

[132] L. B. Ionov, A. P. Korovyakov and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 184 (1979).

[133] J. Ellermann and H. Schössner, J. Organometal. Chem., 166, 31 (1979).

[134] G. S. Harris, I. M. Mack and J. S. McKechnie, J. Fluorine Chem., 11, 481 (1978).

[135] I. Ruppert and V. Bastian, Angew. Chem., 90, 226 (1978).

[136] A. Otero and P. Royo, J. Organometal. Chem., 149, 315 (1978).

[137] S. N. Bhattacharya and M. Singh, Indian J. Chem., Sect. A, 16A, 778 (1978).

[138] P. Choudhury, M. F. El-Shazly, C. Spring and A. L. Rheingold, Inorg. Chem., 18, 543 (1979).

[139] K. Henrick, C. L. Raston, A. H. White and S. B. Wild, Aust. J. Chem., 30, 2417 (1977).

[140] A. J. F. Clark, Diss. Abstr. Int. B., 40, 1706 (1979).

[141] V. V. Klinkova and Yu. A. Pentin, Zh. Prikl. Spektrosk., 30, 325 (1979).

[142] P. Choudhury and A. L. Rheingold, Inorg. Chim. Acta, 28, L127 (1978).

[143] V. E. Khomenko, G. A. Skorobogatov and B. P. Dymov, Zh. Obshch. Khim., 47, 2646 (1977).

[144] F. G. Khalitov, F. D. Yambushev, L. A. Gorchakova, G. M. Doroshkina and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2247 (1979).

[145] R. D. Gigauri, M. A. Indzhiya, B. D. Chernokal'skii and G. N. Chachava, Zh. Obshch. Khim., 48, 809 (1978).

[146] F. M. Khusnutdinova, V. I. Gavrilov, Sh. S. Bikeev and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 383 (1979).

[147] B. A. Arbuzov, Yu. V. Belkin, N. A. Polezhaeva and G. E. Buslaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1146 (1979).

[148] K. Friedrich, W. Amann and H. Fritz, Chem. Ber., 112, 1267 (1979).

[149] G. Cavicchio, M. D'Antonio, G. Gaudiano, V. Marchetti and P. P. Ponti, Tetrahedron Lett., 3493 (1977).

[150] L. P. Filonenko, G. K. Bespal'ko and A. M. Pinchuk, Zh. Obshch. Khim., 49, 2634 (1979).

[151] R. S. Tewari, K. C. Gupta and S. C. Chaturvedi, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 32B, 1165 (1977).

[152] R. S. Tewari and S. C. Chaturvedi, Indian J. Chem., Sect. B., 18B, 359 (1979).

[153] N. A. Nesmeyanov, V. V. Mikul'shina and O. A. Reutov, Dokl. Akad. Nauk SSSR, 237, 1111 (1977).

[154] R. K. Bansal and S. K. Sharma, J. Organometal. Chem., 149, 309 (1978).

[155] G. Fronza, P. Bravo and C. Ticozzi, J. Organometal. Chem., 157, 299 (1978).

[156] A. Strich, Nouv. J. Chim., 3, 105 (1979).

[157] J. Petzelt, K. Kral, N. Rysava, L. Dobiasova, J. Kroupa, J. Oswald, A. Szyszkowski and A. Graja, Solid State Commun., 32, 1315 (1979).

[158] Y. Iida, Bull. Chem. Soc. Jpn., 52, 3101 (1979).

[159] D. B. Chesnut and S. R. Bondeson, J. Chem. Phys., 68, 5383 (1978).

[160] M. H. Abraham and A. Nasehzadeh, Can. J. Chem., 57, 2004 (1979).

[161] J. I. Kim, Z. Phys. Chem. (Wiesbaden), 113, 129 (1978).

[162] T. W. Smith, Diss. Abstr. Int. B., 38, 1218 (1977).

[163] W-t. G. Chan, Diss. Abstr. Int. B., 38, 5375 (1978).

[164] A. J. Ashe, III and W-t. Chan, J. Org. Chem., 44, 1409 (1979).

[165] A. J. Ashe, III, W-t. Chan and T. W. Smith, Tetrahedron Lett., 2537 (1978).

[166] G. Märkl and J. B. Rampal, Tetrahedron Lett., 2569 (1977).

[167] G. Märkl, J. B. Rampal and V. Schöberl, Tetrahedron Lett., 2701 (1977).

[168] G. Märkl and J. B. Rampal, Tetrahedron Lett., 3449 (1977).

[169] G. Märkl and J. B. Rampal, Tetrahedron Lett., 1175 (1978).

[170] G. Märkl and J. B. Rampal, Tetrahedron Lett., 1471 (1978).

[171] G. Märkl and J. B. Rampal, Tetrahedron Lett., 1369 (1979).

[172] G. Märkl, J. B. Rampal and V. Schöberl, Tetrahedron Lett., 3141 (1979).

[173] T. C. Wong and A. J. Ashe, III, J. Mol. Struct., 48, 219 (1978).

[174] T. C. Wong and L. S. Bartell, J. Mol. Struct., 44, 169 (1978).

[175] A. J. Ashe, III, M. K. Bahl, K. D. Bomben, W-t. Chan, J. K. Gimzewski, P. G. Sitton and T. D. Thomas, J. Am. Chem. Soc., 101, 1764 (1979).

[176] T. C. Wong, M. G. Ferguson and A. J. Ashe, III, J. Mol. Struct., 52, 231 (1979).

[177] A. B. Yaroshevskii, V. N. Khlebnikov, V. I. Gavrilov and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 826 (1979).

[178] F. M. Khusnutdinova, V. I. Gavrilov, B. D. Chernokal'skii and V. E. Bel'skii, Zh. Obshch. Khim., 49, 387 (1979).

[179] V. N. Khlebnikov, V. I. Gavrilov and B. D. Chernokal'skii, Zh. Obshch. Khim., 48, 1864 (1978).

[180] V. N. Khlebnikov, V. I. Gavrilov and B. D. Chernokal'skii, Zh. Obshch. Khim., 48, 1581 (1978).

[181] V. N. Khlebnikov, V. I. Gavrilov and B. D. Chernokal'skii, Zh. Obshch. Khim., 49, 822 (1979).

[182] L. I. Zakharkin and N. F. Shemyakin, Izv. Akad. Nauk SSSR, Ser. Khim., 2350 (1977).

[183] L. I. Zakharkin and N. F. Shemyakin, Izv. Akad. Nauk SSSR, Ser. Khim., 1450 (1978).

[184] J. L. Little, Inorg. Chem., 18, 1598 (1979).

[185] A. I. Yanovskii, N. G. Furmanova, Yu. T. Struchkov, N. F. Shemyakin and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1523 (1979).

[186] V. S. Mastryukov, E. G. Atavin, L. V. Vilkov, A. V. Golubinskii, V. N. Kalanin, G. G. Zhigareva and L. I. Zakharkin, J. Mol. Struct., 56, 139 (1979).

[187] R. J. M. Weustink, C. Jongsma and F. Bickelhaupt, Recl. Trav. Chim. Pays-Bas, 96, 265 (1977).

[188] R. J. M. Weustink, R. Laurens and F. Bickelhaupt, Justus Liebigs Ann. Chem., 214 (1978).

[189] R. J. M. Weustink, P. J. A. Geurink and F. Bickelhaupt, Heterocycles, 11, 299 (1978).

[190] H. Vermeer, R. J. M. Weustink and F. Bickelhaupt, Tetrahedron, 35, 155 (1979).

[191] C. H. Stam, Acta Cryst., B36, 455 (1980).

[192] B. A. Arbuzov, E. N. Dianova and N. A. Chadaeva, Dokl. Akad. Nauk SSSR, 246, 1130 (1979).

[193] A. Tzschach and W. Voigtländer, J. Organometal. Chem., 155, 195 (1978).

[194] J. Heinicke and A. Tzschach, J. Organometal. Chem., 154, 1 (1978).

[195] M. S. Bhatia and U. S. Gill, Indian J. Chem., Sect. B, 15B, 1145 (1977).

[196] Yu. G. Bosyakov, B. M. Butin, S. D. Dzhailauov, Z. A. Abramova, A. P. Logunov and S. K. Shishkin, Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR, 46, 125 (1977).

[197] G. Märkl, H. Baier and R. Liebl, Synthesis, 842 (1977).

[198] A. L. Baumstark, M. E. Landis and P. J. Brooks, J. Org. Chem., 44, 4251 (1979).

[199] J. Ellermann, M. Lietz, P. Merbach, G. Thiele and G. Zoubek, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 34B, 975 (1979).

[200] B. J. McKerley, K. Reinhardt, J. L. Mills, G. M. Reisner, J. D. Korp and I. Bernal, Inorg. Chim. Acta, 31, L411 (1978).

[201] H. G. von Schnering, D. Fenske, W. Hönle, M. Binnewies and K. Peters, Angew. Chem., 91, 755 (1979).

[202] M. Baudler and D. Habermann, Angew. Chem., 91, 939 (1979).
a. G. Thiolet, F. Mathey and R. Poilblanc, Inorg. Chim. Acta, 32, L67 (1979).

[203] G. Thiollet, R. Poilblanc, D. Voigt and F. Mathey, Inorg. Chim. Acta, 30, L294 (1978).

[204] D. Seyferth and H. P. Withers, Jr., J. Organometal. Chem., 185, C1 (1980).

[205] D. Hellwinkel, W. Lindner and W. Schmidt, Chem. Ber., 112, 281 (1979).

[206] D. W. Aksnes, K. Bergesen and O. Strømme, *Acta Chem. Scand.*, *A 33*, 413 (1979).

[207] L. Cazaux, J-P. Gorrichon, P. Maroni and J-G. Wolf, *J. Chem. Res.* (*S*), 182 (1979).

[208] C. Anchisi, A. Maccioni, G. Podda and M. Secci, *Rend. Semin. Fac. Sci. Univ. Cagliari*, *48*, 285 (1978).

[209] R. V. Cooney, R. O. Mumma and A. A. Benson, *Proc. Natl. Acad. Sci. USA*, *75*, 4262 (1978).

[210] J. G. Sanders, *Diss. Abstr. Int. B.*, *39*, 5191 (1979).

[211] T. Antonio, A. K. Chopoa, W. R. Cullen and D. Dolphin, *J. Inorg. Nucl. Chem.*, *41*, 1220 (1979).

[212] W. R. Cullen, D. Dolphin, F. W. B. Einstein, L. M. Mihichuk and A. C. Willis, *J. Am. Chem. Soc.*, *101*, 6898 (1979).

[213] R. A. Zingaro, *Environ. Sci. and Technol.*, *13*, 282 (1979).

[214] R. A. Stockton and K. J. Irgolic, *Int. J. Environ. Anal. Chem.*, *6*, 313 (1979).

[215] S. Samman and F. Rolla, *Phosphorus Sulfur*, *4*, 145 (1978).

[216] K. Issleib, A. Tzschach, H. Matschiner, H. U. Block and H. Tanneberg, Ger. (East) 131,065 (1978).

[217] A. Ross, Can. 1,057,296 (1979).

[218] C. P. Smith, Ger. Offen. 2,802,521 (1978).

[219] L. M. Alberino and C. P. Smith, Ger. Offen. 2,802,525 (1978).

[220] B. N. Laskorin, B. D. Chernokal'skii, R. G. Miftakhova, N. P. Stupin, E. K. Ryabova, S. M. Muginova and F. R. Garieva, *Zh. Obshch. Khim.*, *48*, 1088 (1978).

[221] N. G. Zhukova, E. K. Ryabova, V. V. Yakshin, N. P. Stupin, S. M. Muginova and B. N. Laskorin, *Dokl. Akad. Nauk SSSR*, *245*, 1414 (1979).

[222] S. Hiyama, Japan. Kokai, 78, 56,644 (1978).

[223] A. Sakamoto, M. Nishio, Y. Takahashi and T. Okuda, Japan. Kokai 77,133,929 (1977).

[224] Issued to Agence Nationale de Valorisation de la Recherche, Ger. Offen. 2,840,331 (1979).

[225] A. L. Rheingold and J. E. Lewis, U.S. NTIS AD Rep., AD-A049336 (1977).

[226] N. Gamon and C. Reichardt, *Tetrahedron Lett.*, 225 (1979).

[227] G. A. Olah, B. G. B. Gupta and S. C. Narang, *J. Am. Chem. Soc.*, *101*, 5317 (1979).

[228] I. N. Azerbaev, T. A. Yagudeev, A. N. Nurgalieva, G. Dzhakiyaev, R. Kushembaev and T. G. Sarbaev, *Tezisy Dokl. - Vses. Konf. Khim. Atsetilena*, *5th*, 250 (1975).