ARSENIC

ANNUAL SURVEY COVERING THE YEAR 1974

G. O. DOAK AND LEON D. FREEDMAN

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

TABLE OF CONTENTS

1. BOOKS AND REVIEWS

There were no books devoted solely to organoarsenic compounds in 1974. Organoarsenic compounds, however, have been mentioned in several books. In the Chemical Society's *Annual Reports on the Progress of Chemistry* a short

---

Arsenic, Annual Survey covering the year 1973 see J. Organometal. Chem., 89 (1975) 81-150.

section was devoted to organic arsenicals [1]. In a *Specialists Report on Spectroscopic Properties of Inorganic and Organometallic Compounds* [2] numerous references to organoarsenic compounds were scattered throughout the book. Several organic arsenicals that were subjected to X-ray analysis in 1972 have been listed in Volume 5 of *Molecular Structures and Dimensions* [3], and organoarsenic compounds were incidentally mentioned in *Stereochemistry and Bonding in Inorganic Chemistry* [4].

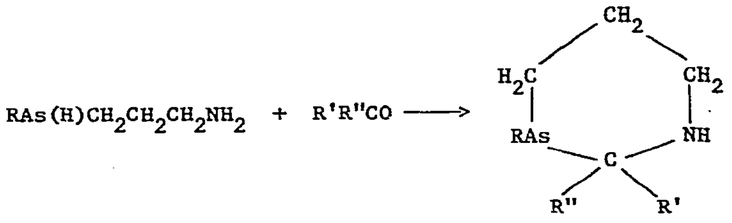
Organoarsenic compounds figured prominently in several review articles. A systematic review of the literature on arsenicals which contained the C≡C bond has been made by Azerbaev and coworkers [5]. A review on molecular structure by diffraction methods [6] included a number of organoarsenic compounds. Reviews on bond strengths [7], heat capacities, phase transitions, and thermodynamic functions [8] of the main group elements included sections on organoarsenic compounds. A review article on the biological effects of organometallic compounds [9] devoted considerable space to arsenicals. A comprehensive survey of the synthesis, preparation, and uses of organoarsenides, -stibides, and -bismuthides has been published [10]. The vibrational spectra of the Group V elements (P, As, Sb, and Bi) have been reviewed by Maslowsky [11]. A review paper on hydroxylamine and oxime compounds containing the As-O and Sb-O bonds has been published by Singh and coworkers [12]. π-Allyl-metal complexes were discussed in a review which included compounds with As-Pd bonds [13]. A general review article on arsenic, antimony, and bismuth organic compounds has been written by Duncan [14]; an article on per- and polyfluorinated aliphatic derivatives of the main group elements contained references to organic arsenicals containing perfluoro groups [15].

A long review article on the reaction of metal complexes of organophosphorus, -arsenic, -antimony, and -bismuth ligands (which the author terms pnictogen ligands) has been published [16]. A number of arsenic-containing ligands, in which arsines and arsine oxides served as ligands to Fe(II), Co(II), and Ni(II), have been discussed in a review paper on coordination chemistry [17].

In a long review paper on cycloalkanes that contained heterocyclic Ge, Sn, or Pb atoms, Pant [18] discussed the reaction of heterocyclic Sn compounds with PCl_3 or $AsCl_3$ to give phosphorins or arsenins. In a review article on ^{13}C NMR spectra of metal carbonyl compounds [19] the ^{13}C spectra of compounds containing Ph_3As, Ph_3Sb, and Ph_3Bi as ligands to such elements as W, Mn, and Rh, were listed.

2. PRIMARY AND SECONDARY ARSINES

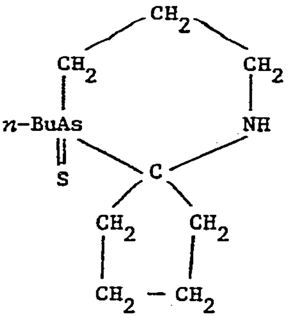
Tzschach and Franke [20] have prepared the two interesting compounds $RAs(H)CH_2CH_2CH_2NH_3Cl$, where R = Ph or *n*-Bu, by the reaction of the corresponding sodium arsenides, RAsHNa with $ClCH_2CH_2CH_2NH_2$. The resulting compounds, $RAs(H)CH_2CH_2CH_2NH_3Cl$ reacted with PhNCO by a reaction, which involved only the amino group, to form the compounds $RAs(H)CH_2CH_2CH_2NHCONHPh$. With bromine or MeI, however, only the arsenic reacted. This difference in reactivity was explained on the hard and soft acid theory. The amines $RAs(H)CH_2CH_2CH_2NH_2$ were treated with ketones to form the cyclic compounds I:



I

A number of such compounds were synthesized in which R = Ph or *n*-Bu and R' and R" were various aliphatic groups or phenyl groups. Again there was a difference in the reactivity of the arsenic and NH groups with PhNCO or with MeI, the NH group reacting with PhNCO and the arsenic with MeI.

Both the acyclic compounds $RAs(H)CH_2CH_2CH_2NH_2$ and the cyclic compounds were readily oxidized. The compounds $Ph\hat{A}s(O)(OH)CH_2CH_2CH_2NH_2$ and $PhAs(S)(SH)CH_2CH_2CH_2NH_2$ and the cyclic sulfide II were prepared in this manner.



II

King and Efraty [21] have reported on the addition of Ph_2MH, where M = P or As, to vinyl isocyanide to produce the expected products $Ph_2MCH_2CH_2NC$. The arsenic compound was prepared with the use of potassium *t*-butoxide, and its IR, NMR, and mass spectra were discussed. A weak molecular ion was observed in the mass spectrum of the arsenic compound but not in the mass spectrum of the phosphorus compound. The use of the two new compounds as ligands with tetracarbonylnorbornadiene-chromium was discussed in some detail.

Byrne and Russ have been interested in the reactions of group Va compounds of the type Me_2SiMMe_2 (M = group Va element) with covalent halides. The present paper by these authors [22] describes the reaction of $(CF_3)_2PH$, $(CF_3)_2AsH$, Me_2PH and Me_2AsH with the compounds Me_2SiMMe_2 (where M = N, P, or As). In the case of $Me_2SiAsMe_2$ and $(CF_3)_2PH$ the following reaction occurs:

$$Me_3SiAsMe_2 + (CF_3)_2PH \xrightarrow{\Delta} Me_3SiF + Me_2AsP(CF_3)_2 +$$

an unidentified product or products

Other reactions which involved arsenicals were as follows:

$$Me_3SiNMe_2 + (CF_3)_2AsH \longrightarrow Me_3SiF + \text{black solid}$$

$$Me_3SiPMe_2 + (CF_3)_2AsH \longrightarrow Me_3SiAs(CF_3)_2 + Me_2PH$$

$$Me_3SiAs(CF_3)_2 + Me_2PH \longrightarrow Me_3SiF + Me_2PAs(CF_3)_2 + \text{brown solid}$$

$$Me_3SiAsMe_2 + (CF_3)_2AsH \longrightarrow Me_3SiAs(CF_3)_2 + Me_2AsH$$

Identification of the products was made by means of NMR spectroscopy.

3, TERTIARY ARSINES

A, Preparation

Contrary to a previous report [23] that $AsCl_3$ formed addition compounds with Ag or Cu, Cartwright and Woolf [24] have shown that with silver an intimate mixture of γ-As, AgCl, and Ag was formed while with copper the mixture consisted of CuCl, β-Cu_3As, and As. The previously reported finding that the addition of PhBr and Mg to these mixtures gave Ph_3As was explained by the following reactions:

$$3\ PhBr + 2\ As \longrightarrow Ph_3As + AsBr_3$$

$$3\ PhBr + Cu_3As \longrightarrow Ph_3As + 3\ CuBr$$

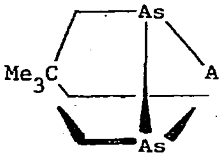
The previous authors [23] had suggested the reaction of PhMgBr with the Ag or Cu complex.

The interesting *cis*-organocyclotriarsane III was prepared by the following synthesis [25]:

$$MeC(CH_2Br)_3 + 3\ NaAsPh_2 \xrightarrow{NH_3} MeC(CH_2AsPh_2)_3 + 3\ NaBr$$

$$MeC(CH_2AsPh_2)_3 + 6\ HI \longrightarrow MeC(CH_2AsI_2)_3 + 6\cdot C_6H_6$$

$MeC(CH_2AsI_2)_3 + 6\ Na \longrightarrow$

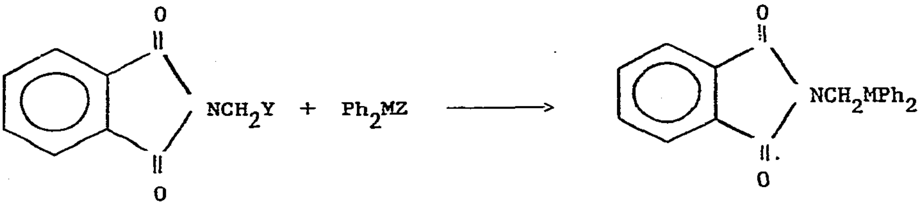


$+ 6\ NaI$

III

Elemental analyses as well as the mass spectrum of III were given and the various fragments in the mass spectrum were tentatively identified. The molecular ion (m/e = 294) had a relative abundance of 100%. The ^1H NMR spectrum gave two singlets (δ = 1.38 for CH_2 and δ = 1.50 ppm for Me relative to TMS). The Raman spectrum was also discussed.

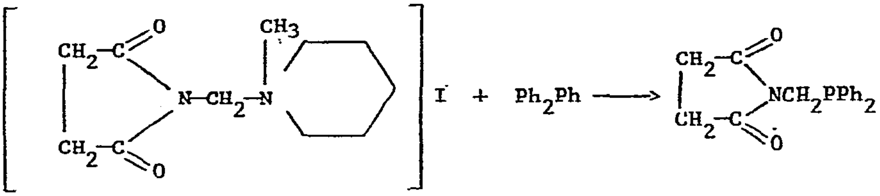
A number of imidomethyl phosphines and arsines have been reported by Tzschach and Kellner [26]. For example the phthalimido compound IV reacts with Ph_2MH as follows:



IV

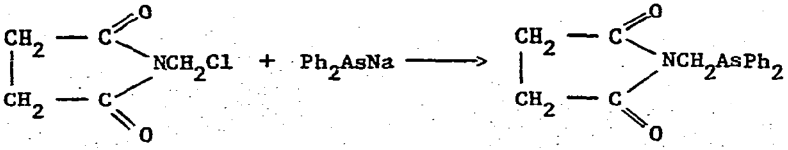
(where Y = NMe_3^+ or Cl, M = P or As, and Z = H or Na)

In a somewhat similar manner V reacted with Ph_2PH:

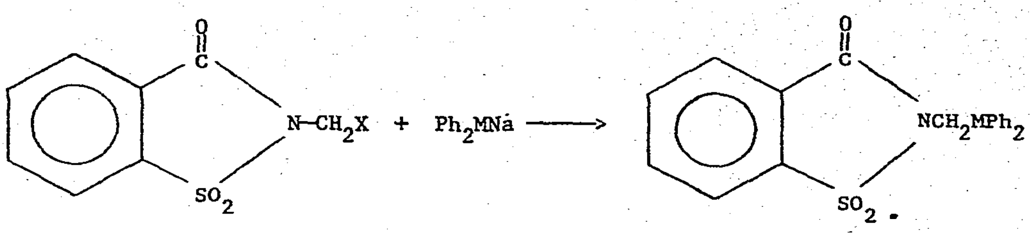


V

The corresponding arsenic compound could not be obtained in this manner but was readily obtained as follows:



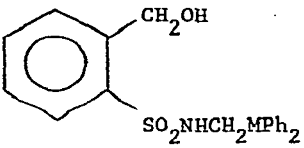
Finally the sulfur compounds VI were prepared:



VI

(where M = As or P)

These latter compounds were reduced with $LiAlH_4$ to give compounds of the type VII.



VII

The phosphorus compound (M = P) was characterized but the arsenic compound (M = As) was not.

Gatilov and coworkers [27] have reported on the isomeric *o*-, *m*-, and *p*-bromophenyl arsines of the type *p*-$MeC_6H_4As(Et)C_6H_4Br$ prepared by the reaction of the appropriate bromophenyl Grignard reagent with *p*-$MeC_6H_4As(Et)Cl$. The arsines were liquids which were characterized only by their IR spectra. The arsines were then oxidized with $KMnO_4$ to the corresponding *p*-$HOOCC_6H_4As(Et)(O)C_6H_4Br$ compounds which were subsequently reduced to the crystalline arsines by means of sulfur dioxide. Again no elemental analyses were given and the compounds were characterized only from their ^1H NMR spectra. The arsines were then resolved into their enantiomers with the aid of quinine. Optical rotations $[\alpha]_D^{20}$ for the *o*-, *m*-, and *p*-bromophenylarsines were found to be +16.80 (-16.20), +15.20 (-14.91) and +13.54 (-13.10) respectively. The explanation for these results was based on hindered rotation of the phenyl groups due to steric inhibition which would decrease in the order *o* > *m* > *p*.

Gatilov and coworkers [28] had previously experienced considerable difficulty in obtaining chiral tertiary arsines containing amino groups in a crystalline state. This difficulty has been overcome by preparing compounds of the type $Et(p\text{-}CH_3C_6H_4)AsC_6H_4NH_2\text{-}p$ or *m*. These formed crystalline diastereomers with (+)-tartaric acid which could be readily separated. The pure enantiomers were then obtained by treatment of the diastereomers with ammonia. The optical rotations $[\alpha]_D^{20}$ for (+) and (-)-$Et(p\text{-}MeC_6H_4)AsC_6H_4\text{-}NH_2\text{-}m$ and for (+) and (-)-$Et(p\text{-}MeC_6H_4)AsC_6H_4\text{-}NH_2\text{-}p$ were +2.21, -1.89, +2.04 and -1.51.

Yambushev, Gatilov, and their coworkers [29] have prepared interesting arsino-substituted anilines of the type $RR'AsC_6H_4NH_2$. These were all obtained by the reaction of $(o\text{-}MeC_6H_4)EtAsCl$ with the lithium reagent $LiC_6H_4NLi_2$, obtained from *o*-, *m*-, or *p*-bromoaniline and excess *n*-BuLi. The resulting compounds $(o\text{-}MeC_6H_4)EtAsC_6H_4NLi_2$ were not isolated but were hydrolysed with dilute HCl to give the desired anilines, *o*-, *m*-, and $p\text{-}NH_2\text{-}C_6H_4As(Et)C_6H_4Me\text{-}o$. They are all high-boiling liquids which decompose on heating and cannot be distilled. They all readily form salts of the type $o\text{-}MeC_6H_4(Et)AsC_6H_4\overset{+}{N}H_3\overset{-}{X}$, where X = Cl, NO_3, or HSO_4. Results of IR spectra as well as elemental analyses and various physical constants for the various compounds were listed.

Having prepared the arsinoanilines of the type $(p\text{-}MeC_6H_4)EtAsC_6H_4NH_2$, Yambushev, Gatilov, and coworkers [30] made use of the free amino group to obtain salts with optically active acids. Thus $(p\text{-}MeC_6H_4)EtAsC_6H_4NH_2\text{-}o$ was heated with (+)-tartaric acid in ethanol and the resulting two diastereomers were separated by fractional crystallization. The two enantiomers were then prepared by hydrolysis of the tartrate salts. The two enantiomers gave rotational values, $[\alpha]_D^{20}$ = + 2.38 (conc. 0.444 in ether) and $[\alpha]_D^{20}$ = − 2.01 (conc. 0.375 in ether).

In addition to the anilino arsines the sulfides o-$MeC_6H_4(Et)As(S)C_6H_4NH_2$ were prepared by heating the free amines (*o*, *m*, or *p*) with S in dry benzene.

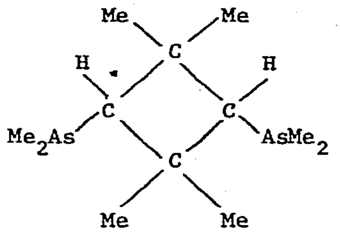
Another method for the preparation of arsino anilines involved protection of the amino group by silylation before the addition of arsine to the system [31]. Thus, the compound $BrC_6H_4N(SiMe_3)_2$ was prepared from Me_3SiCl and $BrC_6H_4N(MgBr)_2$. This latter intermediate, in turn, was prepared by refluxing a bromoaniline with EtMgBr in ether. The bromo compound BrC_6H_4N-$(SiMe_3)_2$ was then converted to the Grignard reagent which was treated with o-$MeC_6H_4(Et)AsCl$ to yield the desired o-$MeC_6H_4(Et)AsC_6H_4NH_2 \cdot HCl$ after treatment of the reaction mixture with HCl. Neutralization of these hydrochlorides and extraction with ether gave the desired anilino compounds. All three compounds, *o*-, *m*- and p-$NH_2C_6H_4As(Et)C_6H_4Me$-o, were obtained in this manner. Physical constants and elemental analyses on the hydrochlorides o-$MeC_6H_4(Et)As$-$C_6H_4NH_2 \cdot HCl$ and on the free amines were given. Some IR data were given.

In addition to (p-$MeC_6H_4)EtAsC_6H_4NH_2$-o, Yambushev, Gatilov, and coworkers [32] have resolved three arsino anilines, (o-$MeC_6H_4)EtAsC_6H_4NH_2$, where the amino group was in *o*-, *m*-, *or p*- position. Again salts of (+)-tartaric acid were used and the diastereomers were separated by fractional crystallization. The enantiomers were then obtained by treatment with aqueous ammonia and extraction with ether. They were obtained as oils with the following optical rotation, $[\alpha]_D^{20}$; *o*-isomer +2.69 and −2.34, respectively; *m*-isomer +2.46 and −2.03, respectively; *p*-isomer +2.24 and −1.72, respectively.

The preparation of several tertiary arsines has been described by Miftakhova and coworkers [33]. Tricyclopentylarsine was prepared from cyclopentylmagnesium bromide and $AsCl_3$. The arsenical Ph_2AsCl and n-C_8H_{17}-$MgBr$ gave $Ph_2AsC_8H_{17}$-n; (n-$C_8H_{17})_2AsBr$ and p-$Me_2NC_6H_4MgBr$ gave n-$C_8H_{17}As$-

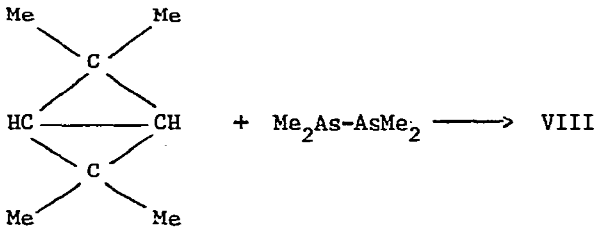
$(C_6H_4NMe_2\text{-}p)_2$, while $(n\text{-}C_9H_{19})_3As$ was prepared from $AsCl_3$ and $n\text{-}C_9H_{19}MgI$. Oxidation of the arsines with H_2O_2 gave the corresponding arsine oxides. The oxides $(n\text{-}C_8H_{17})_2As(O)Ph$, $(n\text{-}C_{12}H_{25})_3AsO$, and $(n\text{-}C_{16}H_{33})_3AsO$ were also reported.

Cullen and Price [34] have described the preparation of an interesting new arsenic ligand 1,3-bis(dimethylarsino)-2,2,4,4-tetramethylcyclobutane VIII.

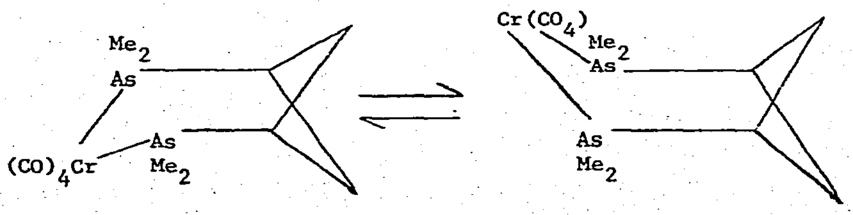


VIII

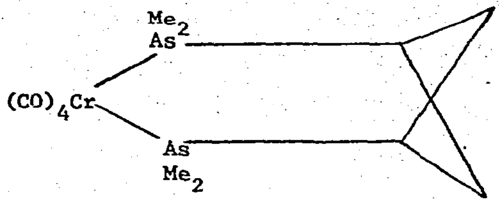
The compound was prepared by the following reaction:



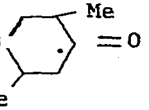
Complexes of this arsine with Cr, Mo, and W carbonyls were described. The ^1H NMR spectrum of the complex $LCr(CO)_4$, where L = the new diarsine, showed only one Me-As resonance and two ring Me resonances. This result could be explained by the following equilibrium in solution:



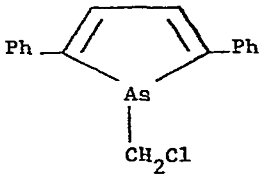
Alternatively the molecule could possess a plane of symmetry (C_{2V} symmetry) as follows:



A crystal structure of this compound showed that it possessed C_2 symmetry (in the solid state) and hence did not agree with the latter suggestion. The authors suggested that the "movement of atoms in solution causes the arsenic methyl groups to become equivalent on a time averaged basis".

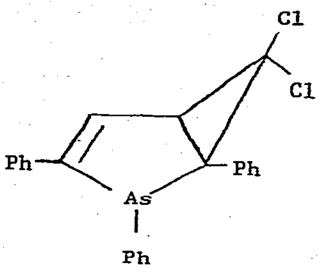
In a Russian patent [35] the compound PhAs  , prepared from $PhAsH_2$ and $MeCH{=}CHCOC(Me){=}CH_2$ was described.

The classical preparation of β-chloropyridine involves the reaction of dichlorocarbene with ring-substituted pyrroles. A similar reaction of dichlorocarbene with 2,5-diphenylarsole led to the formation of 1-dichloromethyl-2,5-diphenylarsole IX [36].

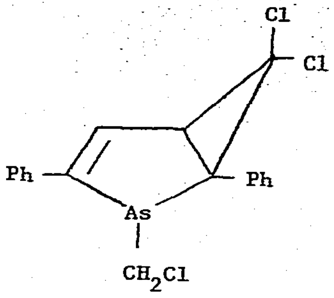


IX

The thermolysis of the adduct X, formed from 1,2,5-triphenylarsole and K *tert*-butoxide in chloroform, gave a high-molecular weight yellow product of unknown composition. The benzyl compound XI on

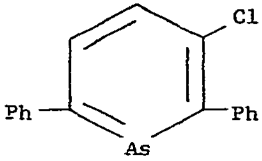


X



XI

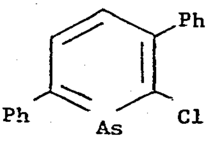
thermolysis gave traces of the desired XII. The principal



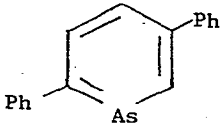
XII

product from the reaction, however, was 2',4'-dichloro-*m*-terphenyl. The reaction of 1-*tert*-butyl-2,5-diphenylarsole with $PhHgCCl_2Br$ in boiling benzene led to the formation of XII in 24% yield.

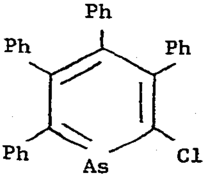
In a second paper [37] from Märkl's laboratory the preparation of the arsenins XIII, XIV, and XV was described.



XIII

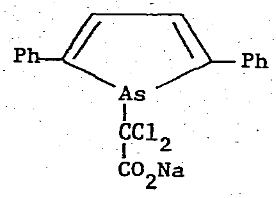


XIV

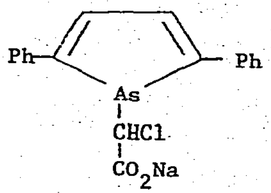


XV

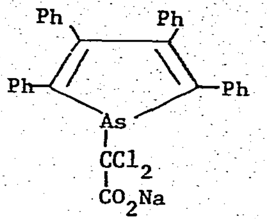
These were prepared by thermolysis of the acetates, XVI, XVII, and XVIII, respectively.



XVI



XVII

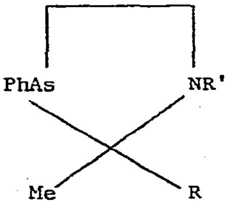


XVIII

The starting materials were obtained from the corresponding 1-lithio derivatives by reaction with sodium di- and trichloroacetates. The products were characterized by U.V. and mass spectral analyses. As is customary in papers from Märkl's laboratory, no elemental analyses were given. An East German patent describes the preparation of compounds of the type $Ph_2As(CH_2)_n$ COR, where R=OH, OEt and NH_2 and n varied from 1 to 3 [38]. An example of the reactions used was as follows:

$$Ph_2AsNa \xrightarrow{ClCH_2CO_2H} Ph_2AsCH_2CO_2H$$

An East German patent covering the preparation of substituted arsazolidines (XIX) for use as fungicides has been reported [39].



XIX

(where R = CO_2H, CH_2CO_2Et, and $CH_2CONHPh$ and R' = H; and where RR' = CH_2CH_2CO). The compound where R = $CH_2CONHPh$ and R' = CONHPh was also prepared.

The interesting quadridentate ligand 1,3-propanebis[(3-dimethylarsinopropyl)phenyl]arsine (XX) has been prepared [40].

$$\mathrm{1,3\text{-}[Me_2As(CH_2)_3As(Ph)]_2CH_2CH_2CH_2}$$

XX

The synthesis involved the following steps:

$$\mathrm{As_2O_3 + ClCH_2CH_2CH_2OH \xrightarrow{NaOH} ClCH_2CH_2CH_2AsO_3H_2}$$

$$\begin{matrix}(1)\\(2)\end{matrix}\ \mathrm{\xrightarrow[SOCl_2]{HCl,\ KI,\ SO_2} ClCH_2CH_2CH_2AsCl_2}$$

$$\mathrm{\xrightarrow{MeMgI} ClCH_2CH_2CH_2AsMe_2}$$

$$\mathrm{PhAsCl_2 + BrCH_2CH_2CH_2Br \xrightarrow{NaOH} PhAs(O)(OH)CH_2CH_2CH_2As(O)(OH)Ph}$$

$$\mathrm{\xrightarrow[SO_2]{HCl,\ KI} PhAs(Cl)CH_2CH_2CH_2As(Cl)Ph}$$

$$\mathrm{Me_2AsCH_2CH_2CH_2Cl \xrightarrow[Et_2O]{Mg} Me_2AsCH_2CH_2CH_2MgCl + 1/2\ PhAs(Cl)CH_2CH_2CH_2As(Cl)Ph}$$

$$\longrightarrow \mathrm{XX}$$

The reactions of this quadridentate ligand with *trans*-Ir(CO)ClAsPh$_3$ as well as the reaction of this iridium compound with several bidentate arsenic-containing ligands were reported.

In a paper largely devoted to the reaction of FeCp(CO)$_2$Cl with tertiary allyl stibines [41], the preparation of CH$_2$=CHCH$_2$AsPh$_2$, and Me(CH$_2$=CHCH$_2$)Ph$_2$-AsBPh$_4$, were described. The reaction of CH$_2$=CHCH$_2$AsPh$_2$ with FeCp(CO)$_2$Cl and NaBPh$_4$ to yield the complex [Ph$_2$As(FeCp(CO)$_2$)$_2$]BPh$_4$ was described. The IR and ^{1}H NMR spectra of this compound was given.

B. Spectra

In an interesting paper Durand and Laurent [42] have compared the chemical shifts of the P-Me and As-Me groups in a series of phosphorus and arsenic compounds, where the compounds were of the types Me_3M, Me_2MOMe, $MeM(OMe)_2$, Me_2MCl, $MeMCl_2$, Me_3MO, $Me_2M(O)OMe$, $MeM(O)(OMe)_2$ and Me_3MBH_3, and where M was either P or As. In the arsines and phosphines the $\Delta\delta$ value, where $\Delta\delta = \delta(As\text{-}Me) - \delta(P\text{-}Me)$, was extremely small (≈ 0.04 ppm) whereas in the esters of the type $(MeO)_nM(O)Me_{3-n}$ it was larger and increased with the number of methoxyl groups attached to the hetero atom ($\Delta\delta = 0.13$ for $n = 0$, 0.37 for $n = 1$ and 0.64 for $n = 2$). This result was explained by $p_\pi\text{-}d_\pi$ bonding between the oxygen and the hetero atom which should be better in the case of phosphorus (2p-3d) than in the case of arsenic (2p-4d). This gave the arsenic a greater positive charge than the phosphorus in such compounds which in turn affects the As-Me less than the P-Me chemical shifts.

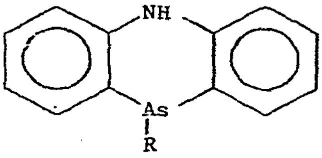
Patterson and Carnevale [43] have reported on the NQR spectra of the 1:1 complexes formed between Me_3In and the trimethyl Group V compounds Me_3N, Me_3P, Me_3As, and Me_3Sb. Quadrupole coupling constants e^2Qq/h and asymmetry parameters η are given. It was concluded that the data was consistent with a small amount of $(d\text{-}d)\pi$ bonding between the Me_3In and the Group V ligands of P, As, and Sb.

The NQR spectra for the ^{35}Cl, ^{75}As, $^{121}Sb/^{123}Sb$ and ^{209}Bi atoms in a series of compounds of the type $(4\text{-}XC_6H_4)_3M$ and $(3\text{-}XC_6H_4)_3M$, where X = H, F, or Cl and M = P, As, or Sb, have been measured by Van der Kelen and De Ketelaere [44] and the data plotted against Hammett σ-constants. The arsenic compounds studied were $(4\text{-}ClC_6H_4)_3As$ and $(3\text{-}ClC_6H_4)_3As$. For every compound studied more than one ^{35}Cl resonance was observed which was explained as being due to intermolecular forces in crystals due to the so-called lattice inequivalence. Usually two such resonances were observed but in a few compounds three resonances were seen. The data suggested that the C-Cl bond increased in ionic character in the order $P \approx As < Sb < Bi$.

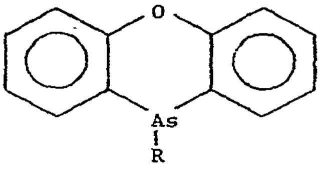
For arsenic (and antimony) compounds the resonance value for Ph_3As was lower than for the substituted tertiary arsines (or stibines). The paper discussed in some detail the type of bonding in the C-M bond without drawing any definite conclusions based on the NQR data.

In an interesting paper Kordosky and coworkers [45] have prepared cobalt complexes of the three ligands $M(CH_2CH_2CH_2AsMe_2)_3$ where M = P, As, and Sb and compared their chemical properties and UV spectra. Thus for the species $[CoLX_2]^+$, the following lowest energy bands were observed for L = $P(CH_2)_3AsMe$ $As(CH_2)_3AsMe_2$, and $Sb(CH_2)_3AsMe_2$, respectively, where the first figure is given in cm^{-1} and the second figure is log ε: X = NCS, 20,830 and 3.35; 19,760 and 3.39, 19,320 and 3.31; X = Cl, 19,600 and 2.92; 18,420 and 2.87, 17,730 and 2.91. A number of other compounds were also listed in which X = Br, I, etc. All such compounds showed a similar decrease in frequency in the order P > As > Sb, and in each case the log ε was in the order P > Sb > As. A number of other complexes of cobalt(III) were also prepared, and UV data were obtained.

UV data for 12 different 5,10-dihydrophenarsazines XXI, the corresponding phenarsazinium iodides, and 10 different 10-H-phenoxarsines XXII were listed and the UV results were correlated with the structures of the compounds [46].



XXI



XXII

(where R was a halogen, an alkyl group, or a substituted aryl group)

It is well known that the *s* and *p* ionization potentials of the central atom X in the series Me_3X, where X = N, P, As, and Sb, decreases in that order. By analogy with the compounds Me_2Y, where Y = O, S, Se, and Te, it was argued [47] that this should lead to an equivalent decrease in the ionization energies of the molecular orbitals involved in the Me_3X compounds. It was found from photoelectron spectra, however, that the lone pair ionization potentials of these compounds were nearly constant. This was explained as involving a change in hybridization; *i.e.*, an increase in *s* character of the central atom in going from N to Sb.

In a more detailed and somewhat longer paper by Debies and Rabalais [48], the photoelectron spectra of compounds of the type Ph_3M, Ph_2MH and $PhMH_2$ were examined (M = N, P, As, or Sb for Ph_3M; M = N, P, or As for Ph_2MH; and M = N or or P for $PhMH_2$). In addition $PhCH_2NH_2$, $PhPCl_2$ and $PhPMe_2$ were also included in the spectral studies. It was concluded that the N non-bonding orbital in phenylamines is more tightly bound than the phenyl π orbitals but in the phenylphosphines, -arsines, and -stibines the non-bonding orbital is at lowest binding energy. The results suggested a shift of electron density from the phenyl groups towards the P, As, and Sb atoms compared with the corresponding N compounds. This, therefore, suggested expansion of the valence shell in the P, As, and Sb compounds to include *n*d orbitals in the molecular bonding. These conclusions were amplified and strengthened by CNDO/2 calculations on $PhNH_2$ and $PhPH_2$.

Zandberg had previously studied the ionization of amines and hydrazines on oxidized tungsten or molybdenum (surface ionization). The ionization occurs at high temperatures (900-1200° K) and the mass spectra of the ions had been studied. The work has now been extended to phosphines (Et_2PH and Et_3P) and the arsines $(n\text{-Pr})_3As$ and $(n\text{-Bu})_3As$ [49]. The mass spectra of the ions were given and pathways for their breakdown in the mass spectrometer were suggested. A comparison of the efficiency of ionization of phosphines and arsines as compared with amines showed that the ionization efficiency was considerably greater in the case of the amines.

The relative ion intensities and the ionization potentials of the triphenyl compounds Ph_3M, where M = N, P, As, Sb, and Bi, were determined by mass spectrometry [50].

De Ketelaere and Van der Kelen [51] have studied the IR and Raman spectra of a group of compounds of the type $(p\text{-}XC_6H_4)_3M$ and $(m\text{-}XC_6H_4)_3M$, where X = F or Cl and M = P, As, Sb, or Bi. Assignments for the various bands were made. A number of fundamental changes in the spectra occurred whether Cl or F was the substituent, but the differences were ascribed to mass differences between the two substituents. Many of the observed bands were found to be insensitive to the nature of the heteroatom. The original paper should be consulted for the various assignments of bands and their variation with the nature of the heteroatom.

C. Use as Ligands

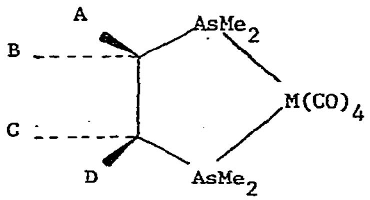
In a long and involved paper Bosnich and coworkers [52] have continued their investigations of the quadridentate ligand "tetars", $Me_2As(CH_2)_3As(Ph)CH_2CH_2\text{-}As(Ph)(CH_2)_3AsMe_2$. This ligand exists in both *meso* and *racemic* forms and the *racemic* form had been previously resolved through the benzoyl-(+) tartaric acid salt. Bosnich and coworkers had also studied the complexes formed from tetars and $CoCl_2 \cdot 6H_2O$ which existed in three different topological forms with the *racemic* ligand and two different topological forms with the *meso* ligand. The present paper describes the preparation and properties of a large number of complexes derived from the already known cobalt complexes, previously described. The *meso*, *racemic* and also the optically active forms of the ligand were used. Both thermodynamic and kinetic methods were used to prepare the various isomers, and the isomeric equilibria were measured in all cases. As had been previously found the *meso* ligand usually preferred a *trans* configuration while the racemic form showed no marked preference for any of the three forms. ^1H NMR data as well as the electronic spectra from 700 to 375 nm were given. Examples of the type of compound prepared were *cis*-β-[Co(R,R:S,S-tetars)CO_3]ClO_4, *cis*-α-[Co(R,R:S,S-tetars)$(OH_2)_2$]$(ClO_4)_3$ and Λ-*cis*-α-[Co(R,R-tetars)$(MeCN)_2$]$(ClO_4)_3$. Other similar complexes contained Cl, Br, CN, NCS, NO_2, and N_3 groups.

In another paper on the subject of cobalt(III) complexes of multidentate arsines, Bosnich and coworkers [53] have used *o*-phenylenebis(dimethylarsine) (termed diars) in preference to tetars because of the complexity of the circular dichroism of the tetars complexes. Complexes of the type $[Co(diars)_2X_2]^+$, where $X^- = Cl^-$, Br^-, I^- and NCS^-, all had the *trans* configuration and while a few *cis* compounds have been made no general method was available. The authors found that *trans*$[Co(diars)_2Cl_2]Cl$ was readily converted into *cis*-$[Co(diars)_2CO_3]Cl$ with Li_2CO_3 which on treatment with perchloric acid gave *cis*-$[Co(diars)(OH_2)_2](ClO_4)_3$. Hydroxide ion converts this latter compound to *cis*-$[C\ (diars)_2OH(OH_2)](ClO_4)_2$. The aquo group in both compounds is quite labile and is easily replaced by a variety of other groups. Thus MeCN and the hydroxyaquo complex gave *cis*-$[Co(diars)_2OH(MeCN)](ClO_4)_2$, while the diaquo complex with MeCN gave *cis*-$[Co(diars)_2(MeCN)_2](ClO_4)_3{\cdot}MeCN$. All of the compounds are subject to substitution and/or isomerization to a greater or lesser degree. Substitution of the diaquo complex with mild reducing anions such as Br^-, I^-, N_3^-, NCS^- and NO_2^- generally led to partial or complete isomerization to the *trans* complex. Recrystallization of nearly pure *cis*-complexes always led to isomerization.

A number of optically active *cis*-complexes were obtained. Thus *cis*-$[Co(diars)_2Cl_2]^+$ ion was resolved with the use of sodium arsenyltartrate and the enantiomers converted to the *cis*-(+ or −)-$[Co(diars)_2(OH_2)_2]^{3+}$ ion with retention of configuration. This diaquo complex could then exchange with NO_2^-, NO_3^-, $CO_3^=$, or OH^- to give the corresponding optically active complexes with full retention of configuration. The rate of isomerization of *cis*-$[Co(diars)_2Cl_2]ClO_4$ was determined and compared with the rate of racemization. The sterochemistry of the complexes was determined largely from NMR data. The authors plan to discuss the CD spectra of these compounds in a later paper.

A number of other papers have appeared from Cullen's laboratory on the structure of heterocyclic rings formed from arsenic-containing chelate compounds and metal carbonyls. Thus Cullen and coworkers [54] have prepared compounds of the type $(CO)_4MAs(Me_2)CH_2CHRCH_2AsMe_2$, where M was Cr, Mo, and W, and where R was H, Me, and *tert*-Bu. The ^1H NMR spectra of these complexes proved to be too difficult to interpret, even with the use of a 222 MHz spectrometer, and as a result the selectively deuterated complexes $(CO)_4MAs(Me_2)CH_2CHRCD_2AsMe_2$, where R = H or *tert*-Bu, were prepared and their deuterium decoupled ^1H NMR spectra were reported. On the basis of these results it was concluded that where R = H the compounds were in an equilibrium between two fast conformational chair forms. Where R = *tert*-Bu, however, the rings were locked in one chair conformation with the *tert*-Bu group in an equatorial position. The synthesis of the arsenical Me_2As-CD_2CH(*tert*-Bu)CH_2-$AsMe_2$ and of the reaction of this compound with $Cr(CO)_6$ were described in detail. Elemental analyses, IR spectra, ^1H NMR spectra (of the dideuterated complexes) and m.p.'s of the various complexes were given.

In a long and somewhat complicated paper Cullen and coworkers [55] considered the structure of the chelate compounds XXIII:

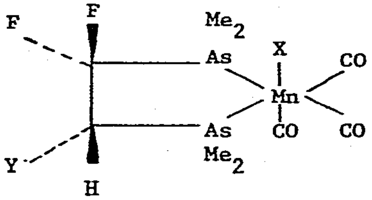


XXIII

(where M = Cr, Mo, and W, and where the groups A, B, C, and D, represent a variety of substituents including Me_3Si, H, F, CF_3, and CN). A total of sixteen new complexes were prepared. These complexes were usually obtained from the necessary bidentate arsenical ligand and the metal hexacarbonyl. Two of the arsenical ligands were new, 1,2-bis(dimethylarsino)-1,1-difluoroethane and 1,2-bis(dimethylarsino)-1,2-difluoroethane, and their preparation from $Me_2AsAsMe_2$ and CH_3CHF_2 and CH_2FCH_2F, respectively, were described in detail. With one exception the new complexes were obtained from the Cr, Mo, or W hexacarbonyls. The exception was 1,2-bis(dimethylarsino)-1-cyano-(tetracarbonyl)molybdenum, which was prepared from 2,5-norbornadiene(tetracarbonyl)molybdenum; this preparation is described in detail. Not all complexes of all of the ligands could be prepared, usually caused by decomposition at the high temperatures used. In some cases the ligands proved difficult to chelate with the metal; in other cases only one arsenic bonded to the metal. Mass, IR and ^1H (and ^{19}F where applicable) spectra were obtained on all of the complexes. The effects produced by varying the solvents, the donor chelate molecule, and the central metal atom were discussed in considerable detail; calculations of the dihedral angles and the coefficients in the Karplus relationships with the various complexes were also described. The results may be summarized by noting that a bulky substituent (Me_3Si) favored the equatorial position on the puckered 5-membered ring; a fluorine atom favored the axial position; and where *dl*-1,2-bis-(dimethylarsino)-1,2-difluoroethane was the ligand, conformations in which the fluorine atoms were *gauche* to each other were preferred.

Another paper from Cullen's laboratory has described the preparation of the ligand $Me_2AsCF_2CHClCF_2AsMe_2$ by UV irradiation of Me_2AsH and Me_2AsCF_2-$CCl{=}CF_2$ [56]. Because of the air-sensitivity of this di-tertiary arsine it was characterized only by its NMR spectra, but complexes formed from carbonyls of Cr, Mo and Mn and the ligand were fully characterized. These complexes $LCr(CO)_4$, $LMo(CO)_4$ and $LMn(CO)_3I$, where L is the bidentate ligand, exist as six-membered rings in two different chair-form conformations. A detailed NMR study was the basis for conformational assignments.

In yet another paper in this series, Cullen and coworkers [57] have prepared a number of complexes of the type XXIV.



XXIV

(where X = Cl, Br, or I, and Y = H or F). The object of this research was stated to be the systematic investigation of the interactions of axial transition metal substituents which are *cis* to a five-membered chelate ring in such complexes as XXIV. The preparation of a typical compound was given and elementary analyses, IR carbonyl stretching frequencies, and both ^{1}H and ^{19}F NMR data (chemical shifts and coupling constants) were given. It appeared that, although changes in the nature of X had little through-bond electronic effect, alternations in the *cis*-axial manganese substituents did produce a marked effect on the conformational preference of the five-membered chelate ring.

In a comprehensive paper, Durig and coworkers [58] have studied the two borane compounds Me_3AsBH_3 and Me_3AsBD_3 and compared the results with those of the corresponding Me_3P and Me_3N adducts. The IR and Raman spectra were taken and assignments of the bands were made. A normal coordinate analysis was done and force constants were calculated. The microwave spectra of $Me_3As^{11}BH_3$, $Me_3As^{10}BH_3$, $Me_3As^{11}BD_3$ and $Me_3As^{10}BD_3$ were recorded from 26.5 to 40 GHz. As-B and As-C distances and the C-As-B angle were calculated. NMR data for Me_3AsBH_3 were also reported. As expected the Me_3AsBH_3 molecule is less stable than the corresponding phosphine and amine complexes as reflected by the force constants.

The Lewis acids BBr_3 and BI_3 formed solid 1:1 adducts with Me_3As and Me_3Sb [59]. The arsenic compound was stable indefinitely at room temperature in an inert atmosphere. Both ^{11}B and ^{1}H NMR spectra were given. In view of the large ^{11}B chemical shift it was possible that these compounds were ionic.

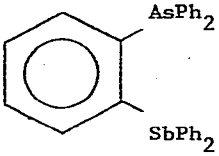
The arsines *o*-$HOOCC_6H_4AsMe_2$, *o*-$HOOCC_6H_4As(C_6H_5Me$-*p*$)_2$, and *o*-$HOOCC_6H_4AsPh_2$ were used as ligands to prepare uranium complexes of the type $[UO_2(OAc)L]_2$, where LH was one of the above arsines [60].

The first report of coordination compounds formed between an arsenic donor compound and a lanthanide element has been given by Dari and Kingston [61]. The complexes $[Ln(As\text{-}N)_5TEF](ClO_4)_3$, where Ln is La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb, As-N is 8-dimethylarsinoquinoline, and TEF is triethyl orthoformate. The evidence for an As-metal bond is based largely on the IR bands associated with the As-Me bond which occur at 887 and 850 cm^{-1} in the free ligand and are shifted to 906, 880, and 850 cm^{-1} for the As-C rocking mode and from 580 and 573 cm^{-1} to 590 and 576 cm^{-1} for the As-Me stretching modes. A band at 284 cm^{-1} in the free ligand assigned to an As-C ring mode was split in the complexes and occurred at 290 and 280 cm^{-1}. The free ligand readily reacted with MeI, whereas the complexes did not. The magnetic properties of the complexes differed considerably from similar complexes containing nitrogen bidentate ligands.

It was found that UV irradiation of $[V(CO)_6]^-$, in the presence of a large series of ligands of the type MR_3 (where M was P, As, or Sb, and R was Ph in the case of As and Sb but a large number of groups where M was P) yielded the mono-substituted complexes $[V(CO)_5MR_3]^-$ [62]. On the basis of ^{51}V NMR and IR data, an attempt was made to classify the ligands according to overall ligand strength. Ph_3As was a less powerful ligand than a number of phosphines but a stronger ligand than other phosphorus ligands and Ph_3Sb.

A new arsenic ligand tris(but-3-enyl)arsine, $(CH_2{=}CHCH_2CH_2)_3As$, was synthesized from the Grignard reagent prepared from 4-chlorobut-1-ene and $AsCl_3$ [63]. The arsine was obtained as an air-sensitive colorless oil which was not characterized, but was converted to the arsonium salt with MeI and this was characterized by elemental analysis. Palladium and platinium complexes of this ligand were prepared and discussed in some detail.

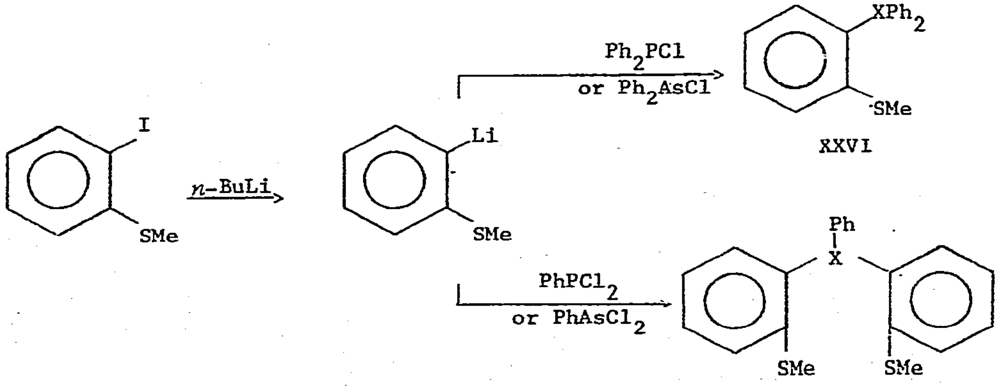
In a paper [64] devoted to nickel(II) complexes of arsines, phosphines, and stibines the synthesis of a number of new *o*-phenylene ligands was given. The only new arsenic-containing ligand was XXV.



XXV

It was readily prepared from *o*-bromophenyldiphenylarsine by conversion to the lithio compound and subsequent treatment with Ph_2SbCl. The majority of the paper deals with the complexes of this and similar compounds with nickel(II).

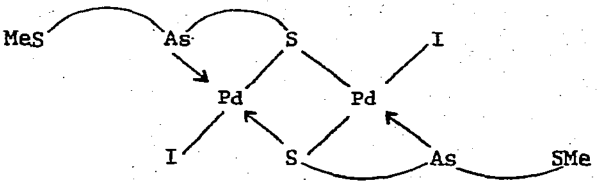
The two phosphorus ligands XXVI and XXVII, X = P, and the two corresponding arsenic compounds, X = As, were synthesized by the following reaction sequence [65]:



XXVI

XXVII

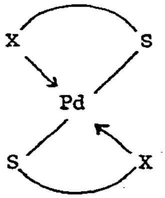
The compounds XXVI acted as bidentate and XXVII acted as tridentate ligands with palladium halides or perchlorates to form compounds of the type $[\mathrm{PdL}]\mathrm{Y}_2$, where Y = I, Br, Cl, or ClO_4. It was found that compounds $[\mathrm{PdL}]\mathrm{I}_2$, where L = XXVI or XXVII, were demethylated on heating in DMF solution. While pure compounds could not be obtained from the two phosphorus compounds or from $[\mathrm{PdL}]\mathrm{I}_2$, where L = XXVI, X = As, a compound was obtained from XXVII, X = As, which was believed to be relatively pure and which was assigned the structure XXVIII:

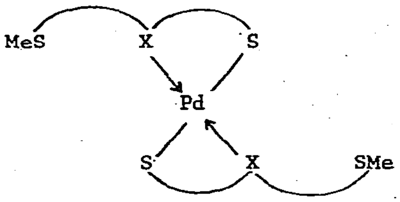


XXVIII

(where the curves represent *o*-phenylene groups)

The four chloro compounds, $[\mathrm{PdL}]\mathrm{Cl}_2$, where L = XXVI or XXVII and X was P or As, were also demethylated. From the compounds where L = XXVI, complexes of the type XXIX were obtained, whereas with the compounds where L = XXVII, complexes of the type XXX were obtained.





XXIX

XXX

(again curved arrows represent *o*-phenylene groups)

In contrast to the halides which were non-electrolytes, the four perchlorate complexes $[\mathrm{PdL}][\mathrm{ClO}_4]_2$ where L = XXVI or XXVII and X = P or As, were di-univalent electrolytes which showed typical conductance in nitrobenzene or nitromethane solutions.

The complexes XXIX and XXX were readily realkylated (or arylated) on the sulfur atoms to give either the original alkylated complexes (when MeBr was used or mixed complexes when *n*-BuBr or *p*-$O_2NC_6H_4Br$ was used). However, not all of the demethylated complexes could be alkylated or arylated on treatment with RX or ArX.

A U.S. patent [66] described the preparation and use as hydrogenation, carbonylation, and carboxylation catalysts of a number of organometallic compounds including the arsenical $EtOHgCO[As(Et_2)C_6H_{11}](CO)_3$, where C_6H_{11} = cyclohexyl.

Bowden and coworkers [67] have described three new bidentate ligands, *viz.* the *ortho, meta, and para* isomers of bis(ditolylarsino)methane. The compounds were prepared by the methods of Hewertson and Watson [68], in which a triarylarsine was cleaved by an alkali metal to form the alkali metal arsenide followed by the reaction of this arsenide with the appropriate alkyl halide, in this case a dihalomethane. The *m*-compound was not obtained in sufficient amounts for further study. The new ligands were characterized only by ^1H NMR data, although m.p.'s were given. The complexes formed between these new ligands and molybdenum hexacarbonyl were described in some detail.

The extremely interesting heterocyclic compound $(CO)_4\underline{CrAsMe_2AsMe_2Cr(CO)_4AsMe_2As}Me_2$ was prepared by Cotton and Webb [69] by the reaction between chromium carbonyl and cacodylic acid. The compound crystallized readily from CH_2Cl_2. An X-ray structure determination demonstrated that the compound existed as a six-membered chair form with the two chromium atoms out of the plane defined by the four arsenic atoms (C_{2h} symmetry). The axial and equatorial Cr-C bond lengths are approximately equal. Although the two methyl groups on arsenic are not symmetry related the room-temperature ^1H NMR spectrum gives only a singlet which broadens as the temperature is lowered to -50°. The true coalesence point, however, could not be determined. A compound with the same empirical formula was prepared by Hayter in 1964 [70] and formulated as a polymer. Cotton and Webb, however, believe the two compounds were identical and that Hayter's molecular weight data were in error.

An interesting group of organo-arsenic compounds has been prepared by Malisch and Kuhn [71]. It had previously been believed that compounds of the type L_nMAsR_2, where M was a transition metal and L was a ligand, could only be obtained where R was a strongly electron withdrawing group such as $CF_3C_6F_5$ or Cl. It has been found by the present authors, however, that compounds of the type $\pi\text{-}C_5H_5(CO)_nMAsMe_2$, where M = Cr, Mo, W, or Fe, were readily obtained by the following reactions:

$$\begin{tikzcd} {[\pi\text{-}C_5H_5(CO)_nM]Na} \arrow[dr, "+Me_2AsCl", "-NaCl"'] & & \pi\text{-}C_5H_5(CO)_nMSiMe_3 \arrow[dl, "+Me_2AsCl"', "-Me_3SiCl"] \\ & \pi\text{-}C_5H_5(CO)_nMAsMe_2 & \end{tikzcd}$$

The resulting compounds were usually stable and could be kept in organic solvents for a considerable time without decomposition. The arsenic atom in these compounds can be readily quaternized with RX, where R may be an alkyl or aryl group, Me_3SiX, or H. If the silyl compounds $\pi\text{-}C_5H_5(CO)_nMSiMe_3$ were treated with Me_2AsCl and RX, the quaternary compound could be obtained directly without having to isolate the intermediate arsines.

In a study of multidentate ligands used to form coordination complexes, the interesting ligands $PhP(CH_2CH_2CH_2AsMe_2)_2$, $PhAs(CH_2CH_2CH_2AsMe_2)_2$, and $o\text{-}Ph_2AsC_6H_4P(Ph)C_6H_4AsPh_2\text{-}o$, were used to form complexes with iridium [72].

In a study of platinum complexes containing phosphorus as a donor atom one organoarsenic-containing complex, namely $PtCl(CH_2CN)(Ph_2AsCH_2CH_2AsPh_2)$ was prepared [73]. Both IR and ^1H NMR data were given.

In addition to the publications discussed above, a large number of other papers have described the use of tertiary arsines as ligands. The metals coordinated to the arsenic in the complexes included chromium [74-77], cobalt [78-86], copper [86,87], gold [85,88-90], iridium [91-100], iron [82,101-104], manganese [105-109], molybdenum [76,77,110,111], nickel [83,86,88,112-115], osmium [116,117], palladium [118-124], platinum [118-121, 125-142], protoactinium [142a], rhenium [109,143-146], rhodium [92,93,95, 100,119,147-153], ruthenium [117, 154-160], silver [161,162], thalium [163], tungsten [76,77,164-166], vanadium [167], and zinc [86].

D. Other Chemical and Physical Properties

Pahil and Sharma [168] have proposed a method for the oxidimetric determination of organic arsines and their complexes, as well as stibines and bismuthines by oxidation with chloramine-T, followed by the addition of KI and back titration of iodine with thiosulfate.

The details of a kinetic study of electronically excited arsenic atoms in $AsCl_3$ and $AsMe_3$ generated by pulsed irradiation were monitored photoelectrically by attenuation of atomic resonance radiation [169].

It has been found by Nefedov, Kolesnikov and Rogozhin [170] that dioxane, in the molecule $C_4H_8O_2 \cdot GeCl_2$, can be replaced by either Ph_3P or Ph_3As simply by boiling the dioxane complex in THF solution in an inert atmosphere with Ph_3P or Ph_3As. The arsenic compound was isolated as coarse white crystals, m.p. 129-132°. No spectral data were given, but the NMR spectrum was stated to show the presence only of aromatic protons.

The heat capacity of Et_3As between 5-60° K (with 36 values given) has been reported by Russian investigators [171].

A German patent described the use of Ph_3As as well as several phosphines as catalysts in the preparation of $MeCO_2CH_2CH{=}CHMe$ and $MeCO_2CHMeCH{=}CH_2$ from $CH_2{=}CHCH{=}CH_2$ and $MeCO_2H$[172].

In an obscure Russian journal the preparation of gallium arsenide GaAs from $GaMe_3$ etherate and AsH_3, Me_3As, or Et_3As was described [173].

Ellermann and coworkers [174] have found that alkyl-arylarsines are selectively cleaved by liquid or gaseous HI in non-aqueous solvents with the

Ph-As bond being cleaved to yield the corresponding alkyliodoarsines. The arsenic compounds investigated were Me_2AsPh, $MeAsPh_2$, $EtAsPh_2$, $(CH_2)_n[AsPh_2]_2$, where n = 1 or 2, and $C[CH_2AsPh_2]_4$. Of interest was the fact that aryl groups were not cleaved from arsines attached to metals:

$$Mo(CO)_5AsPh_3 \;+\; 3\ HI \;\not\longrightarrow\; Mo(CO)_5AsI_3 \;+\; 3\ C_6H_6$$

However, bis(*p*-hydroxyphenyl)arsinic acid was cleaved to yield AsI_3. The reaction may prove to be of considerable value for synthetic purposes. Thus, the tetradentate ligand $C[CH_2AsMe_2]_4$ was readily formed from $C[CH_2AsPh_2]_4$ by cleavage with HI followed by reaction of the resulting iodoarsine with MeMgBr. The mass spectra of the iodoarsines as well as $C[CH_2AsMe_2]_4$ were investigated. Compounds with As-As bonds or $(As)_n$ clusters, where n = 3 or 4, were apparently formed by thermal secondary reactions in the high temperature inlet system of the mass spectrometer. Fragmentation pathways of these cyclic compounds was discussed. The IR spectra of the iodoarsines and $C[CH_2AsMe_2]_4$ were given and assignments of frequencies were made. It was concluded that $EtAsI_2$ existed in *trans* and *gauche* forms.

The cleavage of triphenylphosphine, -arsine, -stibine, and -bismuthine by potassium in liquid ammonia was studied by Rossi and Bunnett [175] and is discussed in detail under Bismuth.

4. AMINOARSINES

The reaction between $(CF_3)_3P$ or $(CF_3)_3As$ with the perfluoro compound $(CF_3)_2NON(CF_3)_2$ led to the cleavage of one of the NO bonds and the formation of perfluorophosphines and arsines [176]:

$$(CF_3)_2NON(CF_3)_2 \;+\; (CF_3)_3M \longrightarrow (CF_3)_2NM(CF_3)_2 \;+\; (CF_3)_2NOCF_3$$

(where M = P or As)

When treated with 20% aqueous NaOH both $(CF_3)_2NP(CF_3)_2$ and $(CF_3)_2NAs(CF_3)_2$

evolve CF_3H. The reaction of $(CF_3)_2NON(CF_3)_2$ with $(CF_3)_3Sb$ takes a different course and is discussed under Antimony. No analyses or spectral data were given.

The reaction of aminoarsines with acids is a well-known method for the preparation of certain types of substituted arsines:

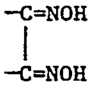
$$X_2AsNMe_2 + 2\ HY \longrightarrow X_2AsY + [NMe_2H_2]Y\downarrow$$

$$X_2AsNMe_2 + HY \longrightarrow X_2AsY + HNMe_2\uparrow$$

(where X = F, Cl, Br, NMe_2, Me, Et, and CF_3 and Y = F, Cl, Br, I, OR, SR, SeR, and NR_2)

The present paper [177] considers the reaction of oxines with Me_2NAsMe_2 to give compounds of the type $RR'C{=}N{-}O{-}AsMe_2$. Fourteen different *o*-(dimethylarsino)oxines of this type were obtained. Physical properties of the compounds (boiling points, IR and ^1H NMR) were given.

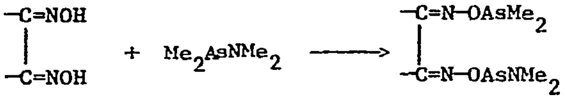
In a long and involved paper Kaufmann and Kober [178] have reported on the reactions of the aminoarsines Me_2AsNMe_2 and $MeAs(NMe_2)_2$ with mono- and bifunctional oximes. For example, oximes of the type



$$\begin{matrix}-C{=}NOH \\ | \\ -C{=}NOH\end{matrix}$$

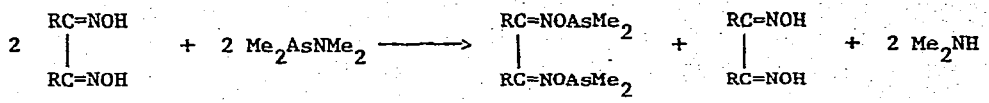
reacted with Me_2AsNMe_2

in a molecular ratio of 1:2 as follows:



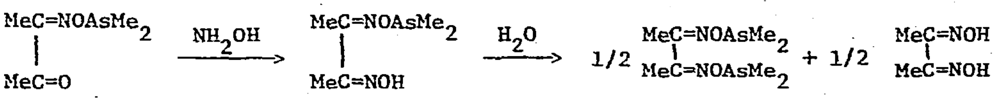
$$\begin{matrix}-C{=}NOH \\ | \\ -C{=}NOH\end{matrix} + Me_2AsNMe_2 \longrightarrow \begin{matrix}-C{=}N{-}OAsMe_2 \\ | \\ -C{=}N{-}OAsNMe_2\end{matrix}$$

Several different oximes were used in this reaction, but benzophenone oxime and benzil dioxime did not react. Oximes and Me_2AsNMe_2 in a molecular ratio of 1:1 reacted in the following manner:



$$2\ \begin{matrix}\mathrm{RC{=}NOH}\\|\\\mathrm{RC{=}NOH}\end{matrix} + 2\ \mathrm{Me_2AsNMe_2} \longrightarrow \begin{matrix}\mathrm{RC{=}NOAsMe_2}\\|\\\mathrm{RC{=}NOAsMe_2}\end{matrix} + \begin{matrix}\mathrm{RC{=}NOH}\\|\\\mathrm{RC{=}NOH}\end{matrix} + 2\ \mathrm{Me_2NH}$$

The tendency to form the di-substituted product is shown by the following reaction:



$$\begin{matrix}\mathrm{MeC{=}NOAsMe_2}\\|\\\mathrm{MeC{=}O}\end{matrix} \xrightarrow{\mathrm{NH_2OH}} \begin{matrix}\mathrm{MeC{=}NOAsMe_2}\\|\\\mathrm{MeC{=}NOH}\end{matrix} \xrightarrow{\mathrm{H_2O}} 1/2\ \begin{matrix}\mathrm{MeC{=}NOAsMe_2}\\|\\\mathrm{MeC{=}NOAsMe_2}\end{matrix} + 1/2\ \begin{matrix}\mathrm{MeC{=}NOH}\\|\\\mathrm{MeC{=}NOH}\end{matrix}$$

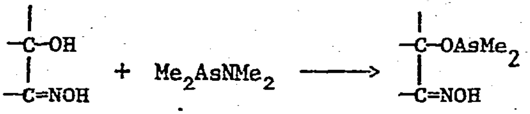
The ketomonooximes MeCOC(NOH)Me and PhCOC(NOH)Me reacted with Me_2AsNMe_2 to give the monooxime compound MeCOC(=$NOAsMe_2$)COMe and MeCOC(=$NOAsMe_2$)COPh. With the aldehyde monooxime RCOC(NOH)H, where R = Me or Ph, neither the spectroscopic results nor the elementary analyses established the structure of the products. Five different ketomonooximes, R_2C=NOH(R=Me, Et),PhCH=NOH, and the two oximes derived from cyclopentanone and cyclohexanone, reacted readily with $MeAs(NMe_2)_2$ to give the compound $MeAs(ON{=}CRR')_2$. However, the two aldoximes MeCH(NOH) and EtCH(NOH) reacted to give products whose structures could not be determined. In the reaction of $MeAs(NMe_2)_2$ with monooximes at room temperature, non-distillable compounds of the type $MeAs(NMe_2)ONCRR'$ were formed. The compounds contained the labile As-N linkage and reacted with compounds containing an active hydrogen (oximes, amines, alcohols, phenols, and thiols) with cleavage of the As-N bond when a 1:1 ratio between the reactants was used.

$$MeAs(NMe_2)ONCRR' + HX \longrightarrow MeAs(X)ONCRR' + HNMe_2$$

However, when an excess of phenol or thiophenol was used both the As-N and As-O bonds were cleaved. For example, the following reaction occurred:

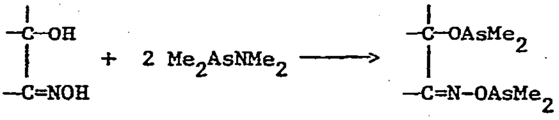
$$MeAs(NMe_2)ONCMe_2 + 2\ PhSH \longrightarrow MeAs(SPh)_2 + Me_2CNOH$$

The reaction of oximes that also contained alcoholic OH groups with Me_2AsNMe_2 occurred as follows, when the reactants were in a 1:1 ratio:



$$\begin{array}{l} | \\ -C-OH \\ \ | \\ -C{=}NOH \end{array} + Me_2AsNMe_2 \longrightarrow \begin{array}{l} | \\ -C-OAsMe_2 \\ \ | \\ -C{=}NOH \end{array}$$

However, when excess Me_2AsNMe_2 was used both OH and =NOH protons were replaced:



$$\begin{array}{l} | \\ -C-OH \\ \ | \\ -C{=}NOH \end{array} + 2\ Me_2AsNMe_2 \longrightarrow \begin{array}{l} | \\ -C-OAsMe_2 \\ \ | \\ -C{=}N-OAsMe_2 \end{array}$$

These two types of reaction occurred with salicylaldoxime but with MeCH(OH)C(NOH)Me both protons were replaced, even when the reactants were in a 1:1 ratio:

$$MeCH(OH)C(NOH)Me + Me_2AsNMe_2 \longrightarrow MeCH(OAsMe_2)C(NOAsMe_2)Me$$

Proton NMR and IR spectra as well as elemental analyses were given for the various compounds prepared. Boiling points (or m.p.'s) for the various compounds were given.

In another paper from Kober's laboratory [179] the reaction of dimethylaminodimethylarsine with 1,2-diols and mercaptols has been investigated. When 1,2-diols and similar compounds react with the arsine in a ratio of 1 diol:2 arsines the following type of reaction occurs:

$$2\ Me_2AsNMe_2 + R_2C(OH)C(OH)R_2 \longrightarrow Me_2AsOCR_2CR_2OAsMe_2$$

The diols used included $HOCH_2CH_2OH$, $Me_2C(OH)C(OH)Me_2$, catechol, 1,2-cyclohexanediol $HOCH_2CH(CH_2Cl)OH$ and $HOCH(Me)CH_2OH$. Other compounds used were $HOCH_2CH_2SH$ and $HSCH_2CH_2SH$. In each case Me_2NH was lost and the product was of the type $Me_2AsX^1CR_2CR_2X^2AsMe_2$, where $X^1 = X^2 = O$ or S, or $X^1 = O$, $X^2 = S$.

When the arsine and the substrates were allowed to react in a ratio of 1:1 the resulting products were of the type $Me_2AsX^1CR_2CR_2X^2H$, where $X^1 = X^2 = O$, or $X^1 = S$, $X^2 = O$. The ^1H NMR and the IR spectra of the compounds were given and commented upon in some detail. Elemental analyses for all of the new compounds were given.

Reaction of the ferrocene compound $C_{10}H_9FeCH_2OH$ (ferrocene methanol) with the aminoarsines Me_2AsNMe_2 and $MeAs(NMe_2)_2$ resulted in splitting of the As-N bond and formation of the ferrocene compounds $C_{10}H_9FeCH_2OAsMe_2$ and $(C_{10}H_9FeCH_2O)_2AsMe$ [180]. When $As(NMe)_3$ was used, an undistillable oil was obtained whose elemental analysis suggested formation of $(C_{10}H_9FeCH_2O)_3As$. ^1H NMR and IR spectra were taken for these compounds but were not discussed extensively.

The reaction of CF_3AsI_2 and CF_3PI_2 with a variety of amines to produce $CF_3P(NR_2)_2$ and $CF_3As(NR_2)_2$ compounds has been described by Adler and Kober [181]. The ^1H NMR and IR spectra of the compounds were discussed in some detail. The P-N and As-N bonds were cleaved by a variety of reagents according to the equation:

$$CF_3E(NMe_2)_2 \ + \ 2\ HX \longrightarrow CF_3EX_2 \ + \ 2\ HNMe_2$$

(where E = P or As and X = Cl, OMe, OPh, SPh, HNC_4H_8NMe, and $HN(C_3H_7)_2$)

5. HALOARSINES

Gigauri and coworkers [182] have found that 1-naphthylmagnesium bromide reacted with As_2O_3 to form, after treatment with hydrochloric acid, the corresponding chloroarsine:

$$4\ \ 1\text{-}C_{10}H_7MgBr \ + \ As_2O_3 \longrightarrow [(1\text{-}C_{10}H_7)_2As]_2O$$

$$[(1\text{-}C_{10}H_7)_2As]_2O \ + \ 2\ HCl \longrightarrow 2\ (1\text{-}C_{10}H_7)_2AsCl \ + \ H_2O$$

Even with a large excess of the Grignard reagent only two naphthyl groups were attached to the arsenic.

Di-1-naphthylchloroarsine failed to react with MeI nor did it react with ethynylbenzene in the absence of a catalyst. It reacted readily, however, with a variety of alkyl Grignard reagents and with phenylmagnesium bromide to form the corresponding tertiary arsines. Elemental analyses, molecular weight data, and m.p.'s were given. A C-As absorption band was assigned to 565 cm^{-1} in the IR spectra of the tertiary arsines.

In continuation of the work reported in the previous paper it was found that p-MeC_6H_4MgBr reacted with As_2O_3 to give, after treatment of the reaction product with HCl, (p-$MeC_6H_4)_2AsCl$ in 61.9% yield [183]. This chloroarsine was then treated with various alkyl Grignard reagents to give a variety of tertiary arsines of the type (p $MeC_6H_4)_2AsR$, where R = Me, Et, *n*-Pr, iso-Pr, *n*-Bu, iso-Bu, *n*-C_5H_{11}, iso-C_5H_{11}, *cyclo*-C_6H_{11}, and $PhCH_2$. The aromatic compound derived from the α-naphthyl Grignard reagent was also prepared. IR spectra, elementary analyses and various physical constants for these compounds were reported.

Laser action was obtained by the photodissociation of a number of organic phosphorus and arsenic compounds, *e.g.* $(CF_3)_2AsI$ and $CF_3(C_2F_5)AsI$ [184]. One organic antimony compound $(CF_3)_2SbI$ also gave such laser action.

The reactions of copper(II) chloride with Ph_3P, Ph_3As, and Ph_3Sb have been studied and reported in two papers from the Slowakischen Technischen Hochschule.

In the first of these papers [185] the absorption band of $CuCl_2$ at 475 nm in acetone was found to change markedly when mixed with Ph_3P or Ph_3As as a function of concentration and time. The curve goes through a maximum and then falls abruptly with increasing Ph_3P concentration. The maximum occurs at a ratio of 1 $CuCl_2$:1 Ph_3P and is interpreted to mean that $CuCl_2$ first forms a 1:1 complex with Ph_3P which then undergoes a redox reaction with reduction of the copper to Cu(I).

A similar plot of absorbance vs. concentration of Ph_3As and $CuCl_2$ in acetone demonstrated that a 1:3 $CuCl_2$-Ph_3As complex was formed followed by reduction of the $CuCl_2$ to CuCl. By contrast Ph_3Sb instantly reduces $CuCl_2$ to CuCl with formation of Ph_3SbCl_2.

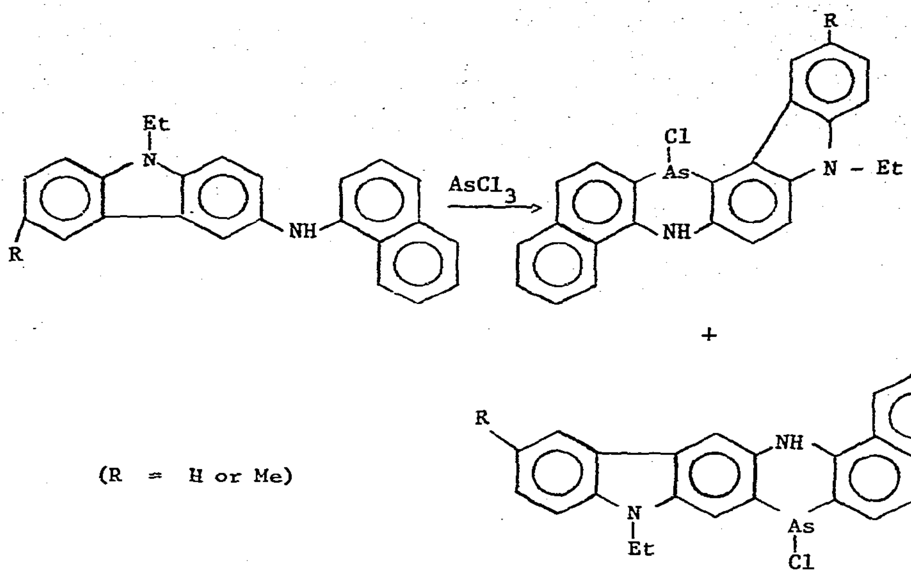
The second paper [186] deals with the isolation of the complexes formed between CuCl and the phosphines, arsines, and stibines, but most of the paper is devoted to the Ph_3P and Ph_3Sb complexes rather than to the Ph_3As complex. The hydrolysis of these complexes was also considered in some detail. Thus in acetone a complex Ph_3PCuCl was formed but in MeCN the complex $(Ph_3P)_3Cu_2Cl_2$ was isolated. In all cases Ph_3PCl_2, Ph_3AsCl_2, and Ph_3SbCl_2 were formed. These complexes were hydrolysed by addition of water to an acetonitrile solution with evolution of HCl corresponding to one half of the chlorine orginally bonded to the copper. The authors suggested the following equation for the reaction of $CuCl_2$ with the triaryl compounds:

$$2\ CuCl_2 + (2+n)Ph_3E \longrightarrow Cu_2Cl_2(Ph_3E)_{n+1} + Ph_3ECl_2$$

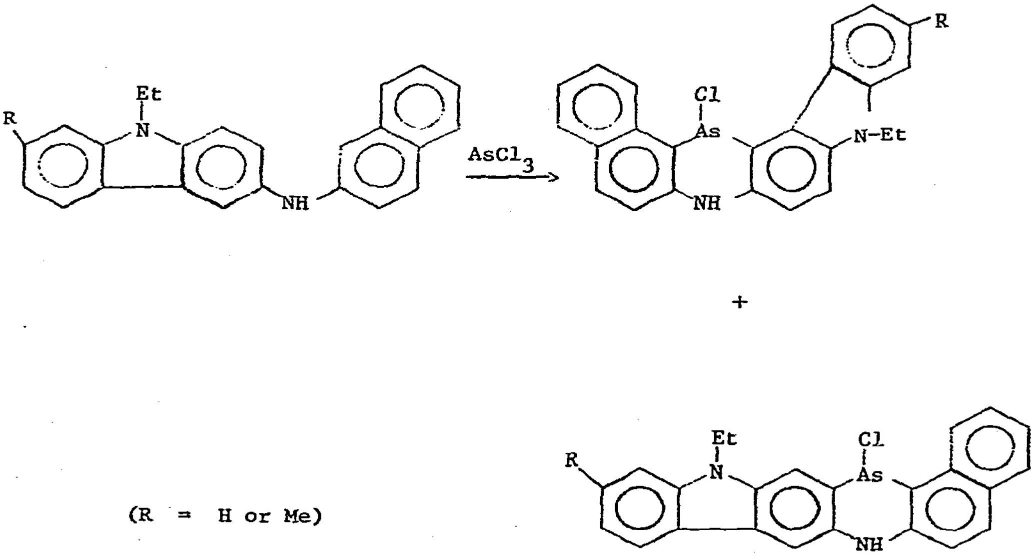
$$(n = 1,2,3,4,\text{ or } 5)$$

The reaction of the arsenic trihalides $AsCl_3$, $AsBr_3$ and AsF_3, as well as $MeAsCl_2$ and Me_2AsCl, with $C_5H_5SiMe_3$ or in some cases with C_5H_5Li (C_5H_5 = the cycopentadienyl group) led to the formation of the cyclopentadienyl arsines $C_5H_5AsX_2$ (X = Br, Cl, or F), $C_5H_5AsMeCl$, and $C_5H_5AsMe_2$ [187]. The arsenicals obtained were viscous liquids, very sensitive to air and moisture. Both IR and ^1H NMR data were given. It was concluded that the cyclopentadienyl group was σ-bonded and that the molecules have a fluxional structure. The rapidity of the metallotropic rearrangements was greatly influenced by the substitutent on the arsenic atom as judged by the ^1H NMR spectra.

In a paper devoted largely to the preparation and biological properties of benzacridines, a number of new dihydroindolebenzophenarsazines were described [188]. The new compounds were obtained as follows:



(R = H or Me)



(R = H or Me)

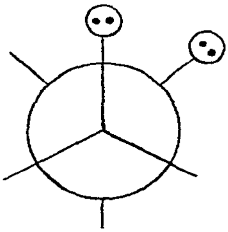
One of the phenarsazines was active against the tubercule bacillus strain 37RV at a minimal concentration of 0.6 γ/ml, but the phenarsazines showed little zoxazolamine hydroxylase inhibiting activity.

In a paper devoted to the NQR spectra of inorganic and organic arsenic compounds [189], the ^{35}Cl and ^{75}As NQR spectra of such organic compounds as $PhAsCl_2$, Ph_2AsCl, Et_2AsCl and Ph_3As, as well as a number of inorganic arsenic compounds, were correlated with structure and with Taft substituent constants.

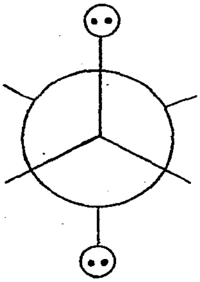
By means of ^1H NMR the equilibrium distributions of fluorine vs chlorine for various organometallic or organometalloid centers were investigated [190]. Although the majority of equilibria studied were between various silicon or phosphorus compounds the preference of fluorine vs chlorine for the system Me_3Ge and Me_2As was studied by mixing Me_2AsF and Me_3GeCl and heating to 120°. The equilibrium was only established after one month and the equilibrium constant obtained was of the order of 10^{-3}, a fact which showed the great preference of F for As as compared with Ge.

6. OTHER TRIVALENT ARSENIC COMPOUNDS

Cowley and coworkers [191] have made use of photoelectron spectroscopy to study rotational isomersisn in diphosphines and diarsines. The two lone electron pairs on the phosphorus or arsenic atoms can be *gauche* or *trans* to each other as shown in the following diagrams:



gauche

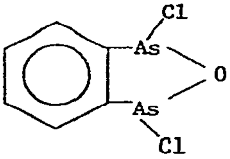


trans

Because of repulsion between the electron pairs one would expect the *trans* configuration to predominate. From the relative peak areas (assigned to *gauche* and *trans* forms) it was possible to compute the percentage of *gauche* and *trans* forms present. In a total of seven compounds the *trans* form always predominated and in one compound, namely $(CF_3)_4As_2$, the *trans* form was present as the sole rotameric form.

In a paper devoted to the preparation and reactions of F_3SiPH_2, it was found that the Si–P bond was split by a variety of reagents [192]. For example, $(CF_3)_2AsI$ reacted slowly with F_3SiPH_2 to yield F_3SiI and $(CF_3)_2AsPH_2$. There was no reaction, however, between F_3SiPH_2 and $(CF_3)_2AsH$.

In a long paper [193] devoted to the mass spectra of an extensive series of *o*-phenylenediarsines and a number of related diamines as well as one stibine, (*o*-dimethylaminophenyl)dimethylstibine, Henrich and coworkers have undertaken a detailed study of the decomposition modes of a number of *o*-phenylenediarsines. The arsenic compounds studied were *o*-$C_6H_4(AsH_2)_2$, *o*-$C_6H_4(AsMe_2)_2$, *o*-$C_6H_4NH_2(AsH_2)$, 3,4-$(AsMe_2)_2C_6H_3Me$, 3,4-$(AsMe_2)_2C_6H_3F$, *o*-$C_6H_4(AsEt_2)_2$, *o*-$C_6H_4(AsHMe)_2$, *o*-$C_6H_4(AsBrMe)_2$, *o*-$C_6H_4(AsMePh)_2$, as well as (*o*-$Me_2AsC_6H_4)_2AsMe$ and the heterocyclic compound XXXI.



XXXI

A comparison was made between the decompositions of the amino compounds and those of the corresponding arsines, and detailed pathways for the decompositions were suggested. These were often substantiated by appropriate metastable peaks. The decomposition of the aromatic diarsines differed considerably from the decomposition of aliphatic diarsines. Cleavage of both arsenic atoms from the aromatic ring and subsequent formation of an As_2 fragment was not observed in non-fluorinated aromatic diarsines.

Although previous workers had investigated by semi-empirical CNDO/2 calculations both phospha- and arsabenzenes (phosphorin and arsenin), the present authors [194] believed that the degree of *d*-orbital participation was greatly overemphasized by this procedure and have done *ab initio* calculations on these two molecules as well as on pyridine. Calculations were made both on the ground state and on some ionized states of these molecules. Tables listing total energies and *d*-populations were given. Among the conclusions drawn was that in pyridine the overall σ-charge on the nitrogen is negative due to electron migration from adjacent CH groups, whereas with phosphorin and arsenin the heteroatoms are overall σ-electron donors to the adjacent CH groups.

Gatilov and coworkers in the USSR have published a number of papers on alkylarylarsenic carboxylates and similar compounds and their resolution into optical antipodes. The present paper [195] was devoted to the synthesis but not the resolution of some formic acid derivatives of the type RArASCOOH where R was an alkyl group and Ar was Ph or *p*-tolyl. A number of nitriles were prepared by metathesis:

$$\text{RArAsX} + \text{KCN} \longrightarrow \text{RArAsCN} + \text{KX}$$

$$(\text{X} = \text{I or Cl})$$

The nitriles were characterized by elementary analyses and the refractive indices, densities, atomic refractions and some IR data were given. Oxidation with H_2O_2 gave the arsine oxides of the formic acid derivatives:

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

These were hygroscopic crystalline solids or sometimes syrups. Reduction of the arsine oxides gave tertiary arsines with some cleavage of the As-COOH bond to form haloarsines. The reducing agent employed was SO_2 (and KI).

The use of aqueous $KMnO_4$ as an oxidizing agent oxidized the *p*-tolyl methyl group to form the compounds $(p\text{-}HOOCC_6H_4)RAs(O)COOH$ which could then be reduced to the corresponding tertiary arsines.

Another method utilized by Gatilov and coworkers [196] involved the reaction of the Grignard-like compounds of the type $R_2AsMgBr$ which can be readily formed from the secondary arsine R_2AsH and an alkyl Grignard reagent:

$$R_2AsH \ + \ R'MgBr \longrightarrow R_2AsMgBr \ + \ R'H$$

This Grignard-like reagent reacted readily with chloroformic esters to form compounds of the type $R_2AsCOOR'$.

Another, and less successful method, involved the reaction of the halides R_2AsCl with Grignard reagents of the type ClMgCOOR, where R = Me, Et, and *n*-Bu. Some IR and molecular refraction data on the new compounds were given. The new compounds prepared were of the type $PhAsR(CO_2R')$, where R = R' = Me; R = Et, R' = Me; R = *n*-Bu, R' = Me; R = Me, R' = Et; and R = R' = Et. The compounds on treatment with alcohol were readily converted to esters of arsinous acids:

$$PhEtAsCO_2Me \xrightarrow{EtOH} PhEtAsOEt$$

Ionov, Gatilov, and coworkers [197] have synthesized the two arsinoformic acids $Ph(R)AsCO_2H$, where R = Me or Et and the ester $(p\text{-}MeC_6H_4)PhAsCO_2\text{-}Me$ as well as a series of other arsinocarboxylic acids of the type $RR'As(CH_2)_nCO_2R''$, where R = Ph, R' = Me, Et, *o*-, or $p\text{-}MeC_6H_4$, R'' = H, Me or NH_2, and *n* = 1 or 2.

One method used for synthesizing these compounds involved the following sequence:

$$PhRAsR' \ + \ BrCN \longrightarrow R'PhAsCN \xrightarrow{H_2O_2} R'PhAs(O)COOH \xrightarrow[+ \ AcOH]{SO_2, H_3PO_3} R'PhAsCOOH$$

The only two compounds synthesized by this method were PhMeAsCOOH and $Ph(p\text{-}MeC_6H_4)AsCOOH$.

A better method for synthesizing these compounds and an essential method for compounds of the type $R_2As(CH_2)_nCOOH$ was as follows:

$$PhR_2As \xrightarrow[NH_3]{Na} PhRAsNa \xrightarrow{X(CH_2)_nCOY} PhRAs(CH_2)_nCOY$$

(where R = alkyl, X = Cl, n = 0, 1, and 2 and Y = OH, OR and NH_2)

Only the IR spectral value for the C=O group was reported but elemental analyses and various physical constants were reported.

In a later paper [198] from Gatilov's laboratory, arsinoformic acids were prepared by the following synthesis:

$$PhRAsNa + CO_2 \xrightarrow{H^+} PhRAsCO_2H$$

(where R = Et or n-Bu)

Esters were obtained by the following reaction:

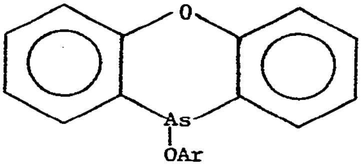
$$PhRAsNa + ClCO_2R' \longrightarrow PhRAsCO_2R'$$

(where R = Et, R' = Me
R = n-Bu, R' = Et)

The esters were obtained as liquids which were distilled *in vacuo* and which were readily hydrolysed by atmospheric moisture. Although morphine or (−)-α-methylbenzylamine did not prove suitable for the preparation of crystalline diastereomers, $PhEtAsCO_2H$ was successfully resolved by the use of quinine. Only the (+)-isomer was obtained in pure form, $[\alpha]_{20}^{D}$ = + 4.72. On heating $PhEtAsCO_2H$ with sulfur, the sulfide $PhEtAs(S)CO_2H$ was obtained.

Unlike amides, acyl derivatives of phosphines, arsines, and stibines gave ^1H NMR spectra which indicated that the protons in the R substituents of $MeCOER_2$(E = P, As, Sb and R = Me or t-Bu) were equivalent over a wide temperature range and hence that the R_2E was not located in the plane of the MeCO group. Further evidence was obtained from the equivalence of the protons in $CF_3COP(CMe_3)_2$ and from the NMR spectra of other acyl phosphines. In the two arsenic compounds studied [199], $CF_3COAs(iso\text{-}Pr)_2$ and $(CF_3)_2CHCOAs(iso\text{-}Pr)_2$, there was also evidence of pyramidal stability ($\Delta G^{\#} > 26.0$ kcal/mole). The authors suggested the possibility of synthesizing optically active acyl arsines with a chiral arsenic atom.

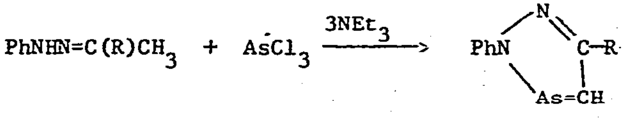
The preparation of a number of 1-aryloxyphenoxarsines of the type XXXII was described by Khusnutdinova and coworkers [200] by the reaction of the corresponding 1-chlorophenoxarsine with a number of substituted phenols.



XXXII

(where Ar = *m*-or *p*-$NO_2C_6H_4$, *m*-or *p*-BrC_6H_4, *p*-FC_6H_4, *m*-or *p*-$MeOC_6H_4$, *m*- or *p*-MeC_6H_4 and *p*-EtC_6H_4)

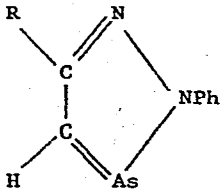
Three new arsadiozoles XXXIII have been reported by Märkl and Martin [201]. They were synthesized according to the following equation:



XXXIII

(where R = Me, Et, and Ph) The corresponding phosphadiozole where R = Ph was also synthesized. The compounds were characterized by UV, IR, ^1H NMR and mass spectra, but no elemental analyses were given. The UV spectra of he diphenyl phosphazole and arsazole as well as the corresponding triazole ere compared. There was a bathochromic shift in going from N to P to As in ne ^{1}La(P) band in the three compounds. These bands were found at 294, 321, nd 352 nm for the three compounds, respectively.

A number of new cycloalkenoarsadiazoles have been reported by Märkl and oworkers [202] by the reaction described in the previous paper. Thus the enzyl compound XXXIV (R = benzyl) was prepared from the hydrazone PhNHN=C(R)- e and $AsCl_3$ and characterized by ^1H NMR and mass spectrometry.

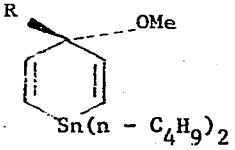


XXXIV

number of similar compounds including bicyclic arsadiozoles obtained from orbornanone phenylhydrazone and one steroid phenylhydrazone were described.

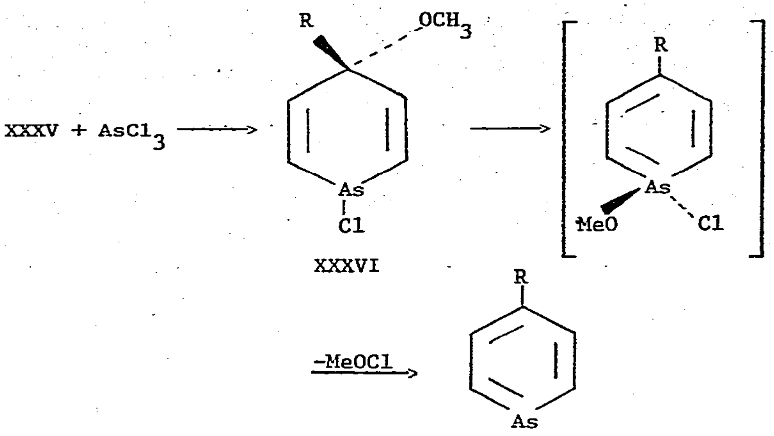
Preparation of three arsabenzenes (arsenins) and one phosphabenzene phosphorin) were reported by Märkl and Kneidl [203]. The arsenins were btained by the reaction of $AsCl_3$ with 4-substituted 4-methoxy-1,4-di- ydrostannins (XXXV).

(R = Ph, *cyclo*-C_6H_{11}, *t* - Bu)



XXXV

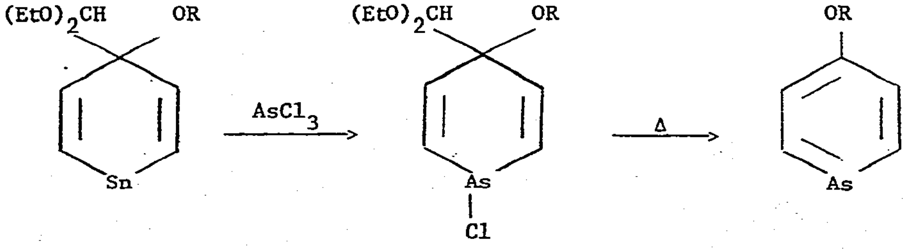
he arsenins were isolated directly, presumably by means of the following echanism:



XXXVI

The compounds XXXVI were detected by NMR spectroscopy but were not isolated from the reaction mixture. The compound MeOCl oxidized the resulting arsenins; yields were significantly increased if the hypochlorite was trapped with triphenylphosphine. The arsenins reacted with such nucleophiles as PhLi to give dihydroarsenins and with dienophiles such as hexafluorobutyne and acetylenedicarboxylic acid esters to give "arsabarrelenes". The arsenins were characterized by mass, UV and NMR spectra but not by the customary elemental analyses.

Märkl has extended the above method to the preparation of alkoxy-substituted arsenins [204]. Thus, by the thermolysis of XXXVII, obtained from the dihydrostannin XXXVIII, he was able to prepare the two alkoxy-substituted arsenins XXXIX:

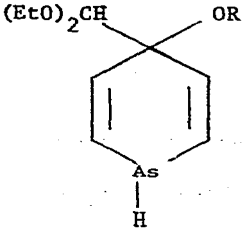


XXXVIII XXXVII XXXIX

(R = Me or Et)

Synthesis of XXXVIII was described. The authors, however, have been unable as yet to cleave the ethers to obtain an hydroxy-substituted arsenin. Both ^{1}H NMR and IR spectra were reported for these two new substituted arsenins.

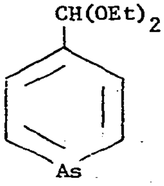
Märkl and Kneidl [205] have attempted to prepare the dihydroarsenins XL by the reduction of the corresponding 1-chloro compounds with a trialkyltin hydride. The compounds XL



XL

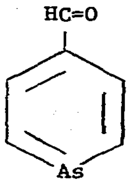
(where R = Me or Et)

could not be detected in the reaction mixtures, however, since they apparently underwent 1,4-elimination of MeOH or EtOH to yield the arsenin XLI.



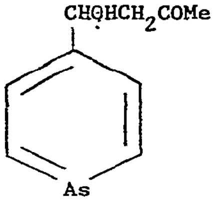
XLI

Under the reaction conditions used for the reduction of the 1-chloro compound, where R = Me, rapid exchange occurred between the diethyl acetal XLI and the MeOH formed in the 1,4-elimination. The PMR spectrum of the reaction mixture indicated that it contained about 50% of the diethyl acetal XLI, 9% of the dimethyl acetal, and 41% of the methyl ethyl acetal. This compound XLI was readily cleaved in moist acetone with an acid ion exchanger to give the aldehyde XLII.

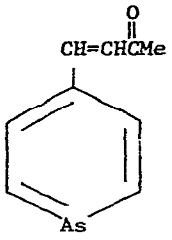


XLII

This aldehyde appears to be a normal aldehyde and undergoes aldol condensation to give XLIII or in the presence of 20% caustic soda and acetone to give XLIV.

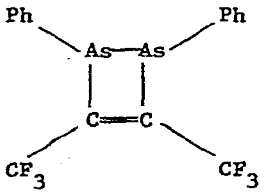


XLIII

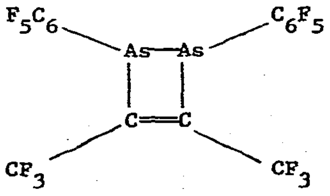


XLIV

In a preliminary communication Bastow and Elmes [206] have reported on the NQR spectra of arsenobenzene $(PhAs)_6$, the fluoro compound $(C_6F_5As)_4$, and two new heterocyclic arsenicals XLV and XLVI.



XLV



XLVI

The latter two compounds were synthesized by the reaction of $(PhAs)_6$ or $(C_6F_5As)_4$ with hexafluorobut-2-yne, but the compounds were not characterized by analytical or spectral data. Since the compound $(PhAs)_6$ was known to exist in a chair form with equatorial phenyl groups, three non-equivalent arsenic sites should be found and these did occur at 60.930, 62.680, and 66.440 MHz in the NQR spectrum. These were run at 298° K. With the fluoro compound $(C_6F_5As)_4$ only two arsenic resonances were found, as expected by symmetry considerations. The NQR spectrum was determined at 298°, 195° and 77° K. The compound XLV showed only one NQR signal, but XLVI gave various frequency absorptions depending upon the method used for its purification. The authors suggested that the compound exists as three different structures but did not speculate on what these structures might be.

A number of physical constants were determined on the compounds RAsO, where R = Me, Et, *n*-Pr and *n*-Bu [207]. These constants were magnetic susceptibility, molecular refraction, dielectric constants, density, index of refraction, ^1H NMR spectra, and ebulioscopic molecular weight determinations in benzene and cyclohexane at several different concentrations. Based on the results of these determinations the authors concluded that EtAsO, *n*-PrAsO and *n*-BuAsO were cyclic trimers whereas MeAsO in solution was a mixture of $(RAsO)_n$ where n = 3, 4, or 5. In the solid state MeAsO existed as a tetramer. There was evidence of limited electron delocalization in the cyclic rings.

Busse, Irgolic, and Dominguez [208] have studied the reaction between lithium diphenylarsenide (from Ph_3As and Li in THF) with benzophenone and with three quinones, anthraquinone, phenanthraquinone, and *p*-benzoquinone. In every case tetraphenyldiarsine was obtained in good yields (51-64%) after hydrolysis of the reaction mixture. Two mechanisms for the reaction were considered, namely the transfer of either one or two electrons from lithium diphenylarsenide to the benzophenone or the quinones. Since a radical anion would be formed by the transfer of one electron, and since EPR signals were detected in the reaction mixture it was decided that a one-electron transfer was involved.

7. ARSONIC AND ARSINIC ACIDS

The IR and Raman spectra of the inorganic ester $(MeO)_3AsO$, and the two organic esters, $MeAsO(OMe)_2$ and $Me_2AsO(OMe)$ were obtained by Vansant and Van der Veken [209] and frequencies were assigned to all of the bands. The ester $Me_2AsO(OMe)$ had not been previously reported. It was prepared via the silver salt technique from $Me_2AsO(OAg)$ and MeI in dry benzene. Normal coordinate analyses were made and structures were assigned to the three esters. It was concluded that the As=O band was > 95% a pure As=O vibration, whereas As-O(C) stretches were strongly coupled with As-C stretches and As-O-C deformations. Force constants for the various bonds were calculated.

A short and preliminary paper by Chatterjee and Sen Gupta [210] gave some crystallographic data on arsanilic (*p*-aminobenzenearsonic) acid. The structure was determined from rotation and Weissenberg oscillation X-ray photographs (some of the crystals, however, appear to be twinned). The crystals are monoclinic and belong to the space group $P2_1$ or $P2_1/m$. The density was found by flotation methods to be in the range 1.85-1.87 g/cm^3 while the calculated density for two formula units per unit cell was 1.83 g/cm^3.

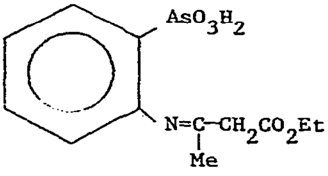
In a paper devoted to the synthesis and toxic properties of amine salts of arsonic acids, Selivanova and coworkers [211] have reported on a number of acid salts of the type $RAsO_3H(H_2NR'_2)$ where R was either an aliphatic or an aromatic group and $R'NH_2$ was an aliphatic amine. Except in one case the authors were unable to prepare the neutral salt, even with a large excess of amine. Toxicity studies were reported on these compounds with salts of $PhAsO_3H_2$ being the most toxic and $p\text{-}CH_3CONHC_6H_4AsO_3H_2$ being the least toxic. Several of the compounds were tested for carcinogenic properties but were found to possess no carcinogenic activity and might have slight antiblastomal activity.

Kinetics of the reaction between Et_2AsO_2Et and EtI have been reported in a Russian article; only the title has been abstracted by *Chemical Abstracts* [212]. The title may contain an error since a paper on the kinetics of the reaction of Et_2AsOEt and EtI has appeared in *Zh. Obshch. Khim.* [213]. The reaction was first order in both reactants but the rates were affected by the purity of the arsenic ester.

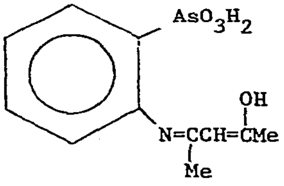
Salts of alkanearsonic acids with tertiary amines have been prepared by reaction of the arsonic acid with a three-fold excess of the tertiary amine [214].

The use of Arsenazo III, carboxyarsenazo, and several other similar types of compounds for indicators in the titration of $SO_4^=$ with $Ba(ClO_4)_2$ in 50% Me_2CO solution at pH 3 was investigated by Zenki [215].

Sandhu and Sandhu [216] have prepared the two new ligands XLVII and XLVIII.



XLVII



XLVIII

They were obtained by condensation of *o*-arsanilic acid (*o*-aminobenzenearsonic acid) with ethyl acetoacetate or with acetylacetone, respectively. Although these two new compounds were not characterized, their coordination compounds formed with Co(II), Ni(II), Cu(II), Zn, and Cd were fully characterized both by elemental analyses and IR spectra. The paramagnetic susceptibility of the

Co, Ni, and Cu complexes were also measured. The complexes with the various metals were discussed in considerable detail, and structural assignments were made.

Interesting complex arylarsonates have been prepared by Sandhu and coworkers [217] by the reaction of dibutyltin oxide with arenearsonic acids. The complexes are of the type $X\text{-}C_6H_4AsO_3Sn(n\text{-}Bu)_2$. The X was H, *p*-Me, *p*-OMe, *o*-OMe, *p*-Cl, *p*-Br, $o\text{-}NO_2$, $o\text{-}NH_2$ and *p*-OH. IR spectra showed no OH stretching bands and in a number of the complexes the As-C(aromatic) stretching frequencies increased by 5–30 cm^{-1} which was taken to indicate coordination of the As–O bond to the tin. Various structures for the different complexes were suggested based on the IR spectral data. Assignments of the various IR bands were made.

The reaction of $2\text{-}Br\text{-}4\text{-}NO_2C_6H_3AsO_3H_2$ with morpholine gave the 2-morpholino-4-nitro acid which could then be reduced to the corresponding 2-morpholino-4-amino compound [218]. A number of derivatives of this acid were prepared by acylation, benzoylation, and other reactions with the free amino group.

Simon and Schumann have published a number of papers on the Raman and IR spectra of alkyl arsonic and arsinic acids and their salts and esters. This is continued in a paper by Gründler, Schumann, and Steger [219] which was devoted to a normal coordinate analysis and a calculation of force constants derived from previously published Raman and IR data on the following species: $MeAsO_3^{2-}$, $Me_2AsO_2^-$, $MeAs(OH)O_2^-$, $MeAs(O)(OMe)_2$, $MeAsO_3H_2$, Me_2AsO_2H, and $Et_2As(OH)_2^+$. Force constants and bond orders were tabulated for the AsO bond in these compounds and the results are correlated with structure. Bond orders were calculated from the force constants. These bond orders differed appreciably from the expected bond orders, and the deviations increased with increasing carbon substitution. Thus the deviations found were AsO_4^{3-}, +2.4%; $C\text{-}AsO_3^{2-}$, -1.5%; $C_2AsO_2^-$, –12.0%. These results were explained mostly by the large electronegativity difference between C and As. The bond orders of the AsO bond were compared with M-O bonds in compounds where M = P, Se and S.

The IR spectra of Me_2AsO_2H in water, in D_2O and as a KI pellet and the Raman spectra in water, D_2O and in the crystalline state have been determined by Vansant and coworkers [220] and assignments of the various bands made based on C_s symmetry for the molecule. A normal coordinate analysis was made by treating the Me and OH groups as single point masses. Internal force constants were given.

In a paper devoted to radical ions derived from electrochemical reduction of a variety of compounds containing such elements as P, As, Si, Mo, and W, Ilyasov and coworkers [221] have described the ESR spectra of radical anions obtained from the organic arsenicals $p\text{-}NO_2C_6H_4As(O)(OEt)_2$, $p\text{-}NO_2C_6H_4AsEt_2$, and $p\text{-}NO_2C_6H_4AsO_3H_2$. The spin density was concentrated mainly on the nitrobenzene moiety with only a small amount on the arsenic. It was also noted that the HFS constants were greater with tetracoordinated arsenic compounds than with the tricoordinated compound. Explanations were suggested for these differences.

The preparation of amidic esters of the type RAs(O)(OR')NR" by means of the following reaction has been reported by Gamayurova and coworkers [222]:

$$RAsO(OR')_2 + R''_2NH \rightleftharpoons RAsO(OR')(NR''_2) + R'OH$$

In order to drive the reaction to the right it was necessary to remove the alcohol continuously, and hence the secondary amine chosen had to boil higher than the alcohol formed in the reaction. The nature of the alkoxy group was also found to influence the ease with which exchange occurred, and amines with longer chains (*n*-Bu) or with branched chains (iso-Pr) were less reactive than shorter chains such as *n*-Pr, Et, or Me. When the amine was $Me(CH_2Ph)NH$ the diamides $EtAs(O)[NMe(CH_2Ph)]_2$ and $PhAs(O)[NMe(CH_2Ph)]_2$ were formed. It was suggested that this diamide formation might be caused by both the greater acidity of the amine and its higher b.p.

The arsonate amides were readily hydrolysed to ammonium hydrogen arsonates:

$$RAsO(OR')(NR''_2) + 2\ H_2O \longrightarrow [RAsO(OH)O][R''_2NH_2] + R'OH$$

IR spectra, elemental analyses and molar refractions for the various amidic esters, and elemental analyses for the ammonium salts were given.

It has been found that turkey poults that received 3-nitro-4-hydroxybenzenearsonic acid from the first day of life suffered histopathological changes and high mortality when the dosage of drug was 100 ppm or greater [223]. In dosages of 200 to 400 ppm the turkeys died within 15 days, whereas those receiving only 50 ppm were essentially the same as untreated controls.

8. TERTIARY ARSINE OXIDES AND RELATED COMPOUNDS

In an excellent paper Carlson and Meek [224] comment on the controversy in the chemical literature regarding the P-chalconide or As-chalconide bond, i.e. the PO, PS, PSe, AsO, AsS, and AsSe bonds. These bonds have been regarded as pure double bonds $P=O$, dative bonds $P\rightarrow O$ or a character intermediate between the two depending on the extent of $p_\pi-d_\pi$ bonding between the P or As and the chalcogen. Although there have been many physical measurements with compounds containing such bonds no definitive dipole moment study has been made, which is the subject of this article. Although most of the compounds studied were phosphorus compounds, some arsenic compounds were studied and the findings with phosphorus could be applied to the arsenic compounds. The conclusions were that the bonds were more polar in the arsenic than in the phosphorus compounds. In the phosphorus series the order of increasing polarity was oxide < sulfide < selenide. From a knowledge of dipole moments, interatomic angles, and bond distances, charge separations $\delta\pm$ for the M-X bond (where M = P or As and X = O, S, or Se) were calculated. For a given group such as Ph, the charge separation produced the trend oxide > sulfide ≈ selenenide. With different groups increasing electronegativity of the group decreased the polarity of the derivatives. Thus the substituent had a marked effect on the amount of p_π-d_π bonding in the P-chalcogen or As-chalcogen bond.

Bravo and coworkers [225] have studied the displacement of the R_3MO grouping in the compounds $R_3MO{\cdot}BF_3$ by similar oxides of the type $R'_3M'O$, as given by the equation:

$$R_3MO{\cdot}BF_3 \;+\; R'_3M'O \rightleftharpoons R'_3M'O{\cdot}BF_3 \;+\; R_3MO$$

(where M = N, P, or As and R and R' were Me, Et, or *n*-Pr)

It was found that the order of displacement was $R_3NO \geq R_3AsO > R_3PO$ which was similar to the order of these oxides as Lewis bases in their complexes with various metal compounds.

In contination of previous studies on polytertiary phosphines and arsines King and Heckley [226] have oxidized the three compounds $(Ph_2PCH_2CH_2)_2PPh$, $(Ph_2PCH_2CH_2)_3P$ and $(Ph_2AsCH_2CH_2)_2PPh$ with both hydrogen peroxide and with elemental sulfur. With the arsenic-containing compound, H_2O_2 gave $(Ph_2As(O)CH_2CH_2)_2P(O)Ph$, but with sulfur only the phosphorus was oxidized to give $(Ph_2AsCH_2CH_2)_2P(S)Ph$. Proton and ^{31}P NMR spectra were reported. IR spectra for the P=O (1180 cm^{-1}) and As=O (884 cm^{-1}) groupings were also reported.

The polarographic reductions of Ph_3PO, *n*-$C_8H_{17}PO$, and Ph_3AsO were compared [227]. Ph_3AsO was unique in that it acted as a strong inhibitor at low concentrations, although it was reduced.

Although the reactions of both anhydrous and hydrated choramine-T with triaryl derivatives of group V elements have been investigated by a number of workers, Padma and coworkers [228] have found that chloramine-T reacted with Ph_3M compounds (M = P, As, Sb, or Bi) in acidified dioxane in a somewhat different manner. While Ph_3P gave Ph_3PO, Ph_3As gave $Ph_3AsO \cdot HCl$, and Ph_3Sb gave Ph_3SbCl_2. The reaction of Ph_3Bi resulted in cleavage of the C–Bi bond. The authors speculated that in each case the Ph_3MCl_2 compound was formed but where M = P or As, the dichlorides were hydrolysed. In each case two equivalents of chloramine-T were consumed per mole of Ph_3M.

Shagidullin [229] has written an interesting paper on the effects of substituents on organophosphorus and organoarsenic compounds on the IR, Raman, and UV spectra of such compounds. The effects of such substituents in *p*-substituted phenylphosphonates and arylarsine oxides of the type R_2ArAsO (where R = alkyl) on the IR P=O and As=O frequencies were correlated with Hammett σ constants.

From UV spectra of these same phosphorus and arsenic compounds as well as from UV spectra of tervalent P and As compounds, the authors concluded that both the P- and As-containing groups, regardless of the valency of the P or As, usually acted as electron acceptor groups.

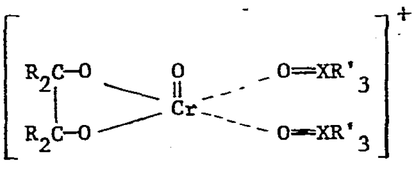
It has been found that perbenzoic acid forms 1:1 crystalline adducts with Ph_3PO, Ph_3AsO and with various pyridine oxides [230]. The adducts were soluble in haloalkanes and were unstable at room temperature. The IR spectra of these adducts indicated that there were strong intermolecular hydrogen bonds in these compounds, somewhat stronger than with benzoic acid and these same Lewis bases.

Milićev [231] has compared the IR and Raman spectra of Ph_3PO and Ph_3AsO with the IR and Raman spectra of a number of Group IV compounds. The spectra were determined both in the solid phase and in benzene solution. Vibrational assignments were made by the use of empirical correlations observed from the large number of Group IV elements studied previously. Frequencies of the X-sensitive bands t, u, and x (Whiffen's nomenclature) were correlated with the reduced masses Ph-X and the electronegativity sums of the substituents.

In a paper [232] devoted to the electrochemical oxidation of Ph_3As in wet acetonitrile in the presence of perchlorate, chloride, and tetrafluoroborate ions, it has been found that with chloride ions the compound formed is $Ph_3AsOHCl$, whereas when perchlorate was used as the supporting electrolyte $(Ph_3AsO)_2HClO_4$ was obtained by the partial reduction of $Ph_3AsOHClO_4$, formed initially by the anodic process. With Et_4NBF_4 the compound obtained was Ph_3AsOBF_3. It was suggested that this was formed by the loss of HF from $Ph_3AsOHBF_4$. In every case cyclic voltammetric curves were given and the peaks in the curves accounted for by the mechanisms suggested for the oxidative steps.

The reactions of Ph_3P, Ph_3As, Ph_3Sb, and Ph_3Bi with bis(trimethylsilyl) peroxide were investigated in a paper devoted to various reactions of this peroxide [233]. Both Ph_3As and Ph_3Sb gave the corresponding oxides, Ph_3AsO and Ph_3SbO, but with Ph_3Bi only the starting bismuthine could be recovered.

An ESR study of several new complexes of chromium with tertiary phosphine and arsine oxides has been reported by Galeev and coworkers [234]. The glycols ethylene glycol and pinacol were also used and took part in complex formation. The arsenicals used were Ph_3AsO in ethylene glycol and pinacol and Et_3AsO in pinacol, and structures were assigned to the complexes on the basis of the ESR data. The general structure of these complexes is shown as XLIX.



XLIX

(where R = Me or H, X = P or As and R' = Ph or Et)

A paper on the two bidentate ligands $Ph_2As(O)CH_2CH_2As(O)Ph_2$ and $Me_2As(O)CH_2CH_2As(O)Me_2$ has been reported by Brisdon and Cocker [235]. With the phenyl compound $[M(Ph_2As(O)CH_2CH_2As(O)Ph_2)_2][ClO_4]_2$ complexes were obtained, whereas with the methyl compound the complexes were of the type

$[M(Me_2As(O)CH_2CH_2As(O)Me_2)][ClO_4]_2$. M was Co, Ni or Cu and IR and visible spectra as well as magnetic susceptibility data were given for all of the compounds. No elemental analyses were given.

Sartorelli and coworkers [236] have described complexes formed between such oxides as Ph_3PO, Ph_3AsO or pyridine oxide and manganese carbonyls. The compounds were either salt-like such as $[Mn(Ph_3AsO)_4I][cis\text{-}Mn(CO)_4I_2]$ or covalent (tetrahedral or octahedral) such as $Mn(Ph_3AsO)I_2$. Both IR and magnetic susceptibility data were given.

Considerable work has been done on tertiary phosphine and arsine oxides, R_3PO and R_3AsO, as donor ligands in coordination chemistry. Laskorin and coworkers [237] have found that the substitution of alkyl groups for Ph groups in the arsine oxides resulted in an increase in the election-donor properties of these compounds. Increasing the length of the alkyl chain also increased the election-donor properties. In these studies phenol was used as the acceptor and the arsine oxides were better electron donors than phosphine oxides.

Several papers have appeared in which triphenylarsine oxide has served as a ligand for gold [238], manganese [239, 240], tungsten [241], and nine lanthanides [242].

9. ARSONIUM SALTS AND ARSENIC YLIDS

The resolution of chiral arsonium salts has been reported by the chemists from Gatilov's laboratory [243]. The compound $p\text{-}MeC_6H_4(iso\text{-}Bu)AsCl$ was converted by KCN into the corresponding cyanide $p\text{-}MeC_6H_4(iso\text{-}Bu)AsCN$. IR spectra on this compound as well as elementary analysis confirmed its structure. Oxidation with $KMnO_4$ converted it to $(p\text{-}HO_2CC_6H_4)(iso\text{-}Bu)As(O)COOH$ together with a complex mixture of products which were difficult to separate. Quaternization with benzylbromide gave $[(p\text{-}HO_2CC_6H_4)(iso\text{-}Bu)C_6H_5CH_2AsCN]Br$. By reaction of this salt with D-(–)-dibenzoyltartaric acid and with L-(+)-dibenzoyltartaric acids, diastereomers were obtained which could be separated by repeated fractional crystallization. By treatment of the diastereomers with NH_4Br in MeOH the pure enantiomers were obtained. $[(+)\text{-}C_6H_5CH_2(\text{iso-Bu})$ $p\text{-}MeC_6H_4AsCN]Br$ gave $[\alpha]_D^{20}$ + 28.16 in methanol. The (–) isomer gave $[\alpha]_{20}^{D}$ = –28.54. The corresponding enantiomeric perchlorates were also prepared and gave $[\alpha]_{20}^{D}$ = +32.70 and –31.20, respectively.

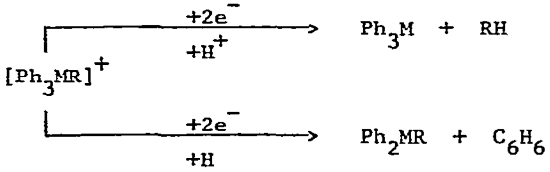
The integral heats of solution ΔH_s of Bu_4PBr, Ph_4PBr and Ph_4AsCl have been determined at various temperatures and at very low concentrations, and the heat capacities of solution at infinite dilution ΔC_p° were derived [244]. These latter values were similar for Ph_4PBr and Ph_4AsCl but different from that of Bu_4PBr. The various possible structures of these ions in solution were discessed in terms of the data.

A paper by Marticorena and Nechtschein [245] deals with the Overhauser effect and exciton motion of the arsonium salt $[Ph_3MeAs]^+(TCNQ)_2^-$ where TCNQ was tetracyanoquinodimethane. A somewhat similar paper by Devreux and Nechtschein [246] has also appeared.

Although ^{60}Co γ irradiation of phosphonium salts was not successful, irradiation of Ph_4As^+ salts gave species corresponding to the Ph_4As species in the ESR spectra of γ irradiated tetraphenylarsonium salts [247]. ESR hyperfine parameters and g-tensor components were listed.

In an interesting paper Tsentovskii and coworkers [248] have compared the conductivities of sodium perchlorate and tetraphenylarsonium iodide, both in acetone. The conductivity of the arsonium salt was also determined in nitromethane. Thermodynamic constants K, ΔG, ΔH, and ΔS for the ionic dissociation processes were calculated and it was shown that there was no difference in principle in the energetics of the dissociation processes between the onium salt and the inorganic salts in acetone solution. The conductivities were shown to be temperature dependent which was attributed to a diminution of the dielectric constant of the solvent with rising temperature. Stokes radii for the ions were also calculated for Ph_4As^+. The Stokes raidus was constant at all temperatures which implied that solvation interaction was absent By contrast, the Stokes radius of Na^+ increased while the radii for I^- and ClO_4^- decreased with rise in temperature. A similar paper dealing with the conductivities of arsonium salts of the type $[Ph_2MeAsR][ClO_4]$ (where R = Et, *n*-Pr, iso-Pr, *n*-Bu, iso-Bu, Me, C_5H_{11}, iso-C_5H_{11}, C_6H_{11} and C_3H_5) in acetone has also appeared [249].

In a short communication Horner and coworkers [250] have reported on various factors which might influence the electrolytic cleavage of alkyltriarylarsonium and alkyltriarylphosphonium salts. The cleavage may occur in two directions:



$$[\mathrm{Ph_3MR}]^+ \xrightarrow[+H^+]{+2e^-} \mathrm{Ph_3M} + \mathrm{RH}$$

$$[\mathrm{Ph_3MR}]^+ \xrightarrow[+H]{+2e^-} \mathrm{Ph_2MR} + \mathrm{C_6H_6}$$

Factors which influenced the direction of cleavage were temperature, cathode material, solvent, and the size of the group R. Thus at 0°, 40° and 80°, the amounts of Ph_3P and Ph_2PMe obtained from $[Ph_3MeP]^+$ with Pb as the cathode material were 2% and 98%, 18% and 82%, and 45% and 55%, respectively. The above results were obtained when water was the solvent. Somewhat different results were obtained when MeOH was the solvent or when Hg was the cathode material. The mechanism for the splitting was believed to be as follows:

$$[\mathrm{Ph_3MR}]^+ \xrightarrow{e^-} .[\mathrm{Ph_3MR}]$$

$$[\mathrm{Ph_3\dot{M}R}] \longrightarrow \mathrm{Ph_2MR} + \mathrm{C_6\dot{H}_5}$$

$$[\mathrm{Ph_3\dot{M}R}] \longrightarrow \mathrm{Ph_3M} + \dot{\mathrm{R}}$$

$$\dot{\mathrm{Ph}} + e^- + H^+ \longrightarrow \mathrm{PhH}$$

$$\dot{\mathrm{R}} + e^- + H^+ \longrightarrow \mathrm{RH}$$

The absorption of the onium salt on the cathode and on the double layer was discussed as a working hypothesis to explain the results. Thus at lower temperatures it was predicted that Ph_2MMe would be the predominate product.

In an article on fluoroimides, Glemser and Höfer [251] have shown that the imide L reacted with Ph_4AsCl to form an arsonium salt:

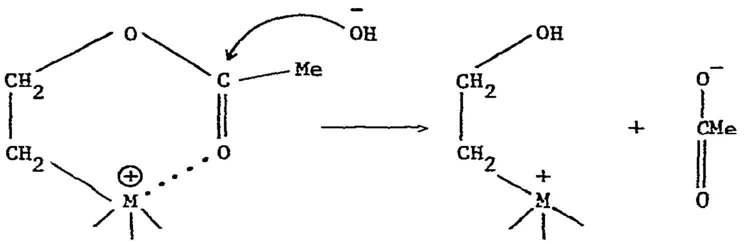
$$\underset{\textstyle L}{HN{=}S(F_2){=}NSO_2F} + Ph_4AsCl \longrightarrow [Ph_4As][N{\equiv}SF_2{=}NSO_2F]$$

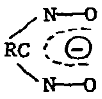
The IR and ^{19}F spectra of the arsonium salt were given.

In an article on force constants and mean amplitudes of vibration of hexahalo ions of Groups IVA and VIA the tetraphenylarsonium ion was among the various cations used [252].

A paper by Gouterman and Sayer [253] is devoted to the solution absorbance and luminescence of tetraphenyl compounds of Group IVA and the tetraphenyl cations of P, As, and Sb. The lowest absorption band of these compounds resembles benzene with one important difference; in benzene the electronic origin is forbidden and all intensity is associated with a symmetric progression built on one mode of asymmetric vibration. In tetraphenyl compounds the asymmetric vibration is relatively unaffected but there is an increasing intensity associated with the symmetric progression built on it in the series $Ph_4Pb < Ph_4Sn < Ph_4Ge < Ph_4Si \leq Ph_4B^- < Ph_4Sb^+ < Ph_4As^+ < Ph_4P^+$. For the cations it is the electronic origin and the progression built on it that give the primary source of intensity. The fluoresence and phosphoresence spectra were also discussed.

The rate constants and activation parameters for the alkaline hydrolysis of a number of ammonium, phosphonium, and arsonium analogs of acetylcholine have been determined by Kunz [254]. The compounds were of the type $[R_3MCH_2CH_2OCOMe]^+X^-$, where R was an alkyl, phenyl, or substituted phenyl group, M was N, P, or As, and X was I or Br. Arsonium compounds prepared were $[\mathrm{Me_3AsCH_2CH_2OCOCH_3}]\mathrm{Br}$ and $[\mathrm{Ph_3AsCH_2CH_2OCOCH_3}]\mathrm{Br}$. With the exception of the two phosphonium compounds the nature of the onium center had very lit influence on the rate of hydrolysis. A mechanism for the hydrolysis was suggested in accord with the experimental results. With the exception of the two phosphonium salts which were cleaved by an addition-elimination mechanis the compounds were believed to be hydrolysed by a mechanism which involved activation of the ester group through a 1,4-interaction of the alkoxy oxygen and the onium center:



It has been found [255] that the nitrosolate ion  can be stabilized by such bulky anions as $\mathrm{Ph_4P^+}$ and $\mathrm{Ph_4As^+}$. Although these compounds are ionic, the corresponding $\mathrm{Ph_4Sb^+}$ can be either ionic or covalent (see the Antimony Section). In a second paper [256] the crystal structure of a $(\mathrm{CH_3})_4$ nitrosolate was determined and the UV, NMR, and IR spectra of a number of other nitrosolates including two arsonium salts were given.

Ion radical salts of arsonium tetracyanoquinodimethane have been widely used in physical studies of ion radicals. Semeniuk and Chesnut [257] have reported on proton spin relaxation times for the ion radical $[\mathrm{Ph_3MeAs}]^+$ $[\mathrm{TCNQ}]_2^-$, where TCNQ = tetracyanoquinodimethane, over the temperature range 90–370° K.

Chernokal'skii and his coworkers have published a number of papers on trialkyl- and triarylalkoxyarsonium salts. Although $[\mathrm{Ph_3AsOCMe_3}]\mathrm{X}$, where X = Cl or Br, have been isolated and characterized [258], attempts to isolate similar compounds have not been successful although their formation as intermediates in the reaction of tertiary arsine oxides with alkyl halides has been postulated. Chernokal'skii and his coworkers [259] have now isolated and characterized by elemental analyses, ^{1}H NMR and IR spectra the compound [Me_3AsOMe]I by the reaction:

$$Me_2AsOMe + MeI \xrightarrow{C_6H_6} [Me_3AsOMe]I$$

It was an extremely hygroscopic compound which reacted with $MeCO_2H$ to form [Me_3AsOH]I; this compound is also found by hydrolysis of the methoxy compound. With Me_3AsO it forms a hydroiodide:

$$[Me_3AsOMe]I + Me_3AsO \longrightarrow 2\ Me_3AsO{\cdot}HI$$

This latter melts at 171-173°, whereas [Me_3AsOH]I melts at 155-156°. In the absence of more definitive data than m.p.'s, the difference between the two compounds would seem to be questionable.

Because of the difficulty in isolating triphenylalkoxyarsonium salts, Abalonin and coworkers [260] attempted the preparation of arsonium salts from Ph_3AsO and haloacetic esters, chloroacetone, and chloroacetonitrile in the belief that the donation of electrons from the carbonyl oxygen or the nitrile nitrogen might stabilize the arsonium salt. Instead they isolated only the triphenylhydroxyarsonium salts, in the cases where the halogens were Cl or Br. With Ph_3AsO and ICH_2CO_2Et either $(Ph_3AsO)_2HI$ or $(Ph_3AsO)_2HI_3$ was isolated. The reactions were also investigated by the use of differential thermal analysis.

The reaction of $EtPh_2AsO$ with a variety of alkyl halides led predominantly to the formation of esters of diphenylarsinous acid together with much smaller amounts of diphenylhaloarsines [261]. The following reactions were suggested to account for the products:

$$EtPh_2AsO + RX \longrightarrow [Ph_2EtAsOR]X \longrightarrow Ph_2AsOR + EtX$$

$$[EtPh_2AsOH]X \longrightarrow [Ph_2As]_2O \longrightarrow Ph_2AsOR + Ph_2AsX$$

In another interesting reaction the authors studied the reactions between Ph_3AsO and haloacetic esters XCH_2CO_2R or between Ph_3AsO and CNCl. It was expected that alkoxyarsonium salts would be formed. However, hydroxyarsonium salts $[Ph_3AsOH]X$ were formed in every case except where an excess of ICH_2CO_2Et was used when the product was $[Ph_3AsO]_2HI_3$. A reaction mechanism to explain these results was suggested.

In previous work [262] on alkoxyarsonium salts of the type $[R_3AsOR']X$, it had been suggested that these might be converted thermally into esters of arsinous acids:

$$PhEt_2AsO + RBr \longrightarrow [PhEt_2AsOR]Br \xrightarrow{\Delta} PhEtAsOR + EtBr$$

The present work [263] showed that the thermal decomposition of hydroxyarsonium salts led to the formation of a number of products. Hydroxyarsonium salts were readily prepared and isolated as crystalline, hygroscopic products. The compounds prepared were $[PhEt_2AsOH]X$, where X = Cl, Br, I; $[Ph_2EtAsOH]X$, where X = Cl and Br (the compound where X = I could not be isolated); and $[(n\text{-}C_3H_7)_3AsOH]X$, X = Cl, Br, and I. The thermal decompositions were carried out in the range 180-200°, and volatile products were collected and many of the products identified in the mixture by their IR spectra. They were unable, however, to isolate pure products by vacuum fractionation. The residue which remained in the flask was identified largely as As_2O_3. Among the identified products in the distillate were alkyl halides, alcohols and dialkylhaloarsines. A complex scheme of thermal decomposition was proposed to account for the products.

The alkali cleavage of allylarsonium salts has been studied by Horner and Samaan [264]. At 70-100° with an excess of NaOH allyltriphenylarsonium salts are cleaved in part to Ph_3As and allyl alcohol. It was suggested that the mechanism involved an S_N2 or S_N2' process. Thus crotyltriphenylarsonium bromide gave 90% Ph_3As and crotyl alcohol with considerable amounts of methylvinylcarbinol. Cinnamyltriphenylarsonium bromide gave 20% of Ph_3As and cinnamyl alcohol but 80% of Ph_3AsO and β-methylstyrene. A number of different allyltriphenylarsonium salts were studied in this manner. The general reaction was as follows:

$$Ph_2R^1AsCH(R^2)C(R^3)=CR^4R^5 \xrightarrow[100^\circ]{OH^-} Ph_2R^1As + HOCH(R^2)C(R^3)=CR^4R^5 + R^2CH=C(R^3)COHR^4R^5$$

The unrearranged product usually predominated. Somewhat different results were obtained at room temperature, in that allyltriphenylarsonium salts with equivalent amounts of alkali were isomerized to the propenyl compounds which then add water to give the 2-hydroxypropyltriphenylarsonium salts. Thus, allyltriphenylarsonium bromide gave $[Ph_3AsCH_2CH(OH)CH_3]Br$ which at higher temperatures with excess alkali gave Ph_3As and acetone.

The cyanolysis of 2-methylallyltriphenylarsonium chloride with KCN gave the salt LI :

$$[Ph_3AsCH_2C(Me)=CH_2]Cl \xrightarrow[H_2O]{KCN}$$

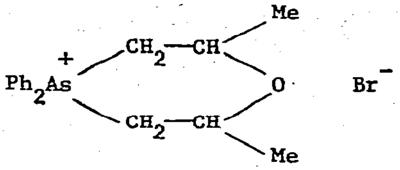
$$Ph_3As + \underset{\text{LI}}{[Ph_3AsCH_2C(Me)_2CN]Cl} + CH_2=C(Me)CH_2OH$$

The salt LI was hydrolysed by aqueous alkali to LII:

$$[Ph_3AsCH_2C(Me)_2COOH]Cl$$

LII

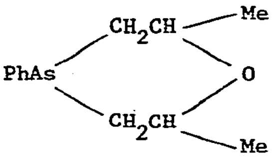
Allyltriphenylarsonium salts reacted with methanolic or ethanolic NaOH to give compounds of the type $[Ph_3AsCH_2CH(OR)CH_3]X$, where R = Me or Et. These were cleaved by 10% NaOH to Ph_3As and $CH_2=C(OR)CH_3$. In a continuation of this work Horner and Samaan [265] have shown that diallyldiphenylarsonium bromide reacted with aqueous sodium hydroxide to give a mixture of propenyldiphenylarsine (18%), 2-hydroxypropyldiphenylarsine (31%), and the arsonium salt LIII.



LIII

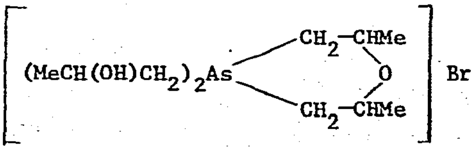
Diallylmethylphenylarsonium bromide reacted in a similar fashion to give the corresponding methylphenyl compounds. If diallyldiphenylarsonium bromide was allowed to react with 2% aqueous NaOH for 14 days the yield of LIII increased to 90%. A detailed mechanism for the formation of LIII was suggested. Evidence for the mechanism was obtained by synthesizing several of the intermediates in the reaction scheme and showing that these could be converted to LIII by aqueous sodium hydroxide. Electrolytic reduction of LIII gave the arsine LIV, as well as $Ph_2AsCH_2CH(OH)CH_3$ in 28% and 65% yields, respectively. With HBr, LIII gave the arsonium salt $[Ph_2As(CH_2CHBrCH_3)_2]Br$.

In addition to diallyldiphenyl- and diallylmethylphenylarsonium bromide, the reactions of triallylphenyl- and tetraallylarsonium bromides with aqueous alkali were investigated.



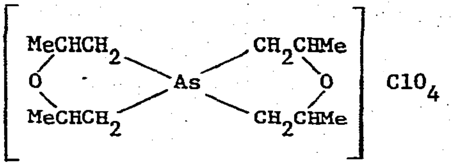
LIV

The triallylphenyl salt gave the cyclic arsine LIV, while the tetraallyl salt gave compound LV at 100°.



LV

The arsonium salt LVI (isolated as the perchlorate) was obtained by the interaction of tetraallylarsonium bromide and aqueous alkali for 120 hours at room temperature.

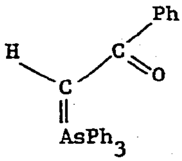


LVI

In addition to the above arsonium salts the reaction of diallyldiphenylphosphonium bromide with aqueous alkali was investigated.

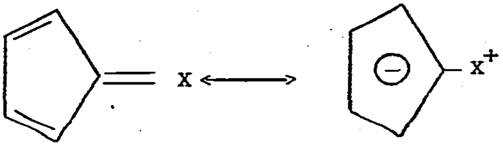
In an interesting reaction Wolfsberger [266] has shown that the imines $R_3P{=}NSiMe_3$ reacted with R'_2PCl to give phosphonium salts of the type $[R_3P{=}NP(R')_2PR'_2]Cl$. In a similar manner with R''_2AsCl the compounds $[R_3P{=}NP(R')_2AsR''_2]Cl$ were obtained. The ^1H-decoupled ^{31}P NMR spectra of the compounds prepared were discussed in considerable detail. The ^1H NMR spectra were also considered.

The conformations of a number of phosphorus and arsenic ylids have been determined by means of dipole moment studies by Lumbroso and coworkers [267]. The arsenic compounds studied were $Ph_3As{=}CHCOMe$, $Ph_3As{=}CHCOPh$, $Ph_3As{=}CHCOC_6H_4Ph\text{-}p$, $Ph_3As{=}CHCOC_6H_4Me\text{-}p$, $Ph_3As{=}CHCOC_6H_4NO_2\text{-}p$, $Ph_3As{=}CHCO_2Me$, and $Ph_3As{=}NC_6H_4NO_2\text{-}p$. It was found, for example, that the compounds of the type $Ph_3CHCOC_6H_4Y$, where Y = H, Ph, Me, or NO_2, all possessed the *cis*-structure in benzene solution:



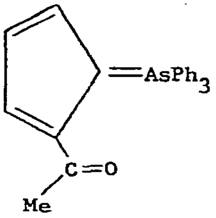
The polarities of the P=C, As=C, P=N, and As=N bonds were also determined from the dipole moment data.

The dipole moments of a number of sulfonium, phosphonium, arsonium, and stibonium cyclopentadienylides have been determined by Lumbroso and coworkers [268]. The contribution of the ionic canonical form in the following scheme increased in the order S < P < As:



(where X = an alkyl- or aryl-substituted sulfonium, phosphonium, arsonium or stibonium group)

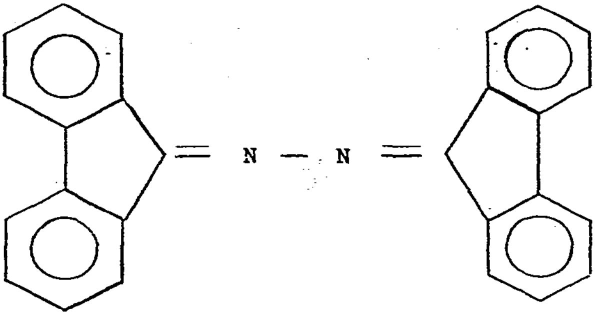
The dipole moment of the stibonium ylid was abnormally small (2.2D for triphenylstibonium tetraphenylcyclopentadienylide compared with 7.75D for the corresponding phosphonium and 8.82D for the corresponding arsonium compounds.) The dipole moment of the interesting compound LVII was determined and was believed to exist exclusively in the *cis* form LVII.



LVII

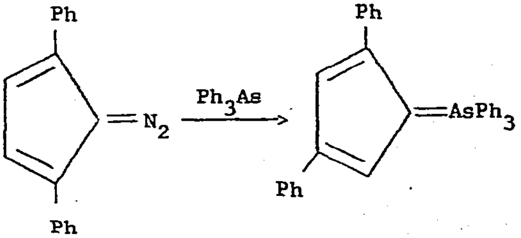
The dipole moment of the stibonium ylid is also considered in the Antimony section.

A number of papers have previously appeared from Lloyd's laboratory on cyclopentadienylides. The present paper [269] is concerned with the preparation and spectral properties (UV and ^{1}H NMR) of a number of phosphonium, sulfonium, and arsonium ylids. A method for the preparation of 3,4,5-triphenylphosphonium cyclopentadienylides was found. The method was also successful for the preparation of triphenylarsonium 2-benzyl-3,4,5-triphenylcyclopentadienylide, but was not successful for the preparation of a number of other arsonium phenyl-substituted cyclopentadienylides. The method involved the decomposition of diazocyclopentadienes in the presence of Ph_3P or Ph_3As. It was found, however, that the addition of copper-bronze catalysed the reaction and that the desired arsonium cyclopentadienylides could be thus prepared. The use of this catalyst allowed the reaction to be carried out at much lower temperatures; *e.g.* in refluxing benzene, cyclohexanol, or ethanol. Several reactions, however, gave unexpected results. Thus diazofluorene and Ph_3As gave the ketazine LVIII rather than the arsonium ylid.

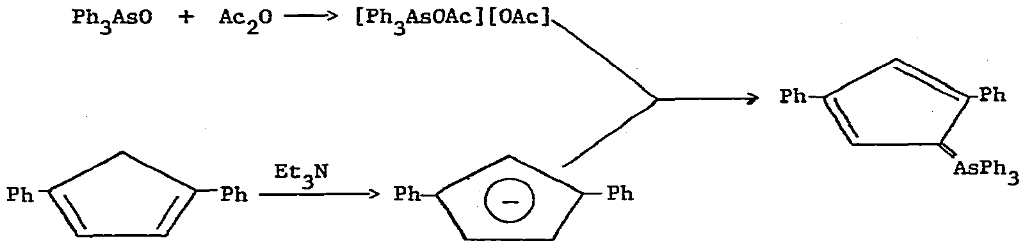


LVIII

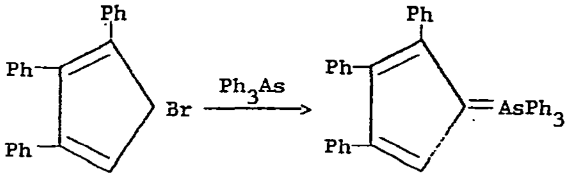
An even more unexpected result involved the reaction of 2,5-diphenyldiazocyclo pentadiene with Ph_3As:



As shown in the above equation, there is a migration of a phenyl group from the 5- to the 4-position. A mechanism for this migration was suggested. The 2,4-compound was also prepared by the following independent route:



A method in which 3,5-dibromocyclopentene reacted with Ph_3As to replace the bromine atoms by the triphenylarsine moiety [270] has now been adapted to the preparation of arsonium triphenylcyclopentadienylides from bromotriphenylcyclopentadiene:

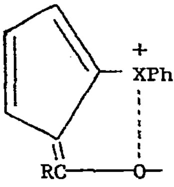


Triphenylphosphine, however, did not give the ylid but rather the reaction underwent photodebromination.

The UV spectra of the di- and triphenylcyclopentadienylides closely resembled the spectra of the corresponding, previously reported, tetraphenyl analogs. It was found that triphenylarsonium and 2,4-diphenyl- and 2,3,5-triphenylcyclopentadieylides underwent a small bathochromic shift in the longest wavelength absorption maximum in CH_2Cl_2 when this solvent was used in place of methanol. This solvatochromism had previously been observed only with pyridinium, bismuthonium, and telluronium cyclopentadienylides.

The triphenylarsonium cyclopentadienylides reacted with *p*-nitrobenzaldehyde to give the expected fulvenes. The corresponding phosphonium compounds did not react under these circumstances.

Acetylation of both the phosphonium and arsonium 2,3,4-triphenylcyclopentadienylides yielded acetyl compounds with the acetyl group in the 5-position. With 2,4-substituted ylids the triphenylphosphonium compound was acetylated in either the 3- or the 5-position, whereas the arsonium compound was acetylated only in the 5-position, although the product was contaminated with high molecular weight impurities. It was interesting to note that the C=O stretching frequency of the 2(5)-acetyl substituted products was extremely low (1560-1570 cm^{-1}), a fact which was attributed to contributions from the canonial form LIX.



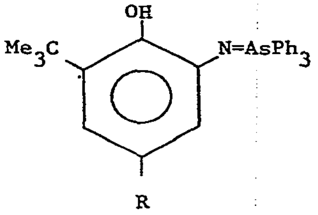
LIX

(where X = P or As)

The Vilsmeier method was used for formylating both the phosphonium and arsonium ylids. Triphenylarsonium 2,3,4-triphenylcyclopentadienylide formed a stable 5-formyl derivative, but the 2,3,5-triphenyl compound gave a formyl derivative which could not be purified, although mass spectral data indicated that the 4-formyl compound was formed.

Diazonium salts were found to couple readily with substituted (as well as unsubstituted) phosphonium and arsonium cyclopentadienylides. Triphenylarsonium 3,5-diphenylcyclopentadienylide gave the 2-phenylazo derivative; the 2,4,5-triphenyl cyclopentadienylide gave the 3-phenylazo derivative. It was concluded that electrophilic substitution occurred preferentially in the 2(5)-position but when these positions were blocked the 3(4)-position could be attacked. NMR spectra of the acid salts of the phosphonium and arsonium cyclopentadienylides were obtained although the salts themselves were not isolated and characterized.

In a paper devoted largely to N-(hydroxyphenyl)iminophosphoranes, the arsenic compounds LX were described [271].

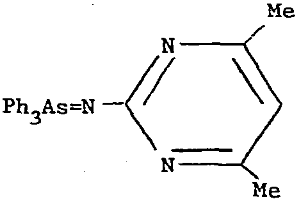


LX

(R = t-C_4H_9 or CPh_3)

The compounds were obtained by the reaction of 2-NH_2-4R-6-t-BuC_6H_2OH with Ph_3AsBr_2. These two compounds, as well as a number of similar phosphorus compounds, were transformed into the corresponding radicals by the action of light or oxidizing agents. Both the ESR and ENDOR spectra of these compounds were obtained. Large ^{75}As (as well as large ^{31}P) coupling constants were obtained. By consideration of both the coupling constants and the lack of hyperfine splitting components caused by the aromatic substituents, it was concluded that conjugation across the heteronuclei seemed prohibited.

In two long and involved papers Cadogan and Gosney outline the preparation of triarylarsinimines $R_3As=NX$ and the possible use of triarylarsines as traps for nitrenes. In the first paper [272] the preparation of a number of triarylarsinimines was described. Photolysis of phenylazide in the presence of Ph_3As did not lead to the formation of any arsinimine, but pentafluorophenylazide in Ph_3As at 120° gave $Ph_3As{=}NC_6F_5$. In a similar reaction 2-azido-4,6-dimethylpyrimidine reacted with Ph_3As at 120° in the presence of copper bronze to give LXI.



LXI

p-Nitrophenylazide, in wet dioxane, again in the presence of copper bronze, gave a hydrated arsinimine which was formulated as *p*-$NO_2C_6H_4NHAs(OH)Ph_3$. The authors were unable to obtain an arsinimine from *p*-cyanophenylazide and Ph_3As. Other azides reacted with Ph_3As to give the arsinimines $Ph_3As{=}NCO_2Et$, $Ph_3As{=}NCN$, and $Ph_3As{=}NSO_2C_6H_4Me$-*p*.

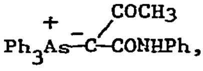
In reactions of Ph_3As with non-azide compounds, 3-phenyl-1,4,2-dioxazolidin-5-one and the corresponding *p*-nitrophenyl compound gave, in the presence of copper bronze, $Ph_3As{=}NCOPh$ and $Ph_3As{=}NCOC_6H_4NO_2$-*p*, respectively. The arsinimine $Ph_3As{=}NCO_2Et$, previously prepared from Ph_3As and ethyl azidoformate, was also obtained from $EtO_2CNHOSO_2C_6H_4NO_2$-*p* and Ph_3As in the presence of Et_3N. Finally the arsinimine $Ph_3As{=}NSO_2C_6H_4Me$-*p* (previously prepared from chloramine-T and Ph_3As) was obtained from Ph_3As and *p*-$MeC_6H_4SO_2N_3$ or from Ph_3As and *p*-$CH_3C_6H_4SO_2NHOSO_2C_6H_4NO_2$-*p*.

In the second paper of this series Cadogan and Gosney [273] investigated the reactions of Ph_3As with acyl, sulfonyl, and phosphinyl amides in the presence of lead tetraacetate. Some previous authors have suggested that amines are oxidized by lead tetraacetate to nitrenes, although this observation could not be confirmed by other workers. Since the present authors had shown that Ph_3As was a good trapping agent for nitrenes, they now investigated the reaction of amines with lead tetraacetate in the presence of Ph_3As and indeed demonstrated that arsinimines were formed:

$$RNH_2 \xrightarrow{Pb(OAc)_4} RN: \xrightarrow{Ph_3As} Ph_3As{=}NR$$

That the reaction did not proceed by this mechanism, however, was demonstrated by the lack of reaction of RNH_2 with $Pb(OAc)_4$ in the absence of Ph_3As, and the authors demonstrated that an arsenic diacetate was formed as an intermediate:

$$Ph_3As \xrightarrow{Pb(OAc)_4} Ph_3As(OAc)_2 \xrightarrow{RNH_2} Ph_3As{=}NR$$

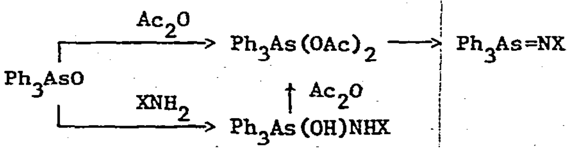
The diacetate could actually be isolated and characterized, and was then shown to react with $MeSO_2NH_2$, *p*-$MeC_6H_4SO_2NH_2$, and $PhCONH_2$ to form arsinimines. *p*-$NO_2C_6H_4CONH_2$ reacted only at higher temperatures (boiling CH_2Cl_2) to form the arsinimine. The authors also demonstrated that $Ph_3As(OAc)_2$ was an intermediate in the reaction of Ph_3AsO with acetic anhydride and $MeCOCH_2CONHPh$ to form the ylid,  $\overset{+}{Ph_3As}{-}\overset{-}{C}(COCH_3){-}CONHPh$, by showing that the diacetate formed the ylid by reaction with $MeCOCH_2CONHPh$ in boiling benzene.

The authors then extended the reaction of Ph_3AsO with Ac_2O to demonstrate that the resulting $Ph_3As(OAc)_2$ would react with amides to form arsinimines:

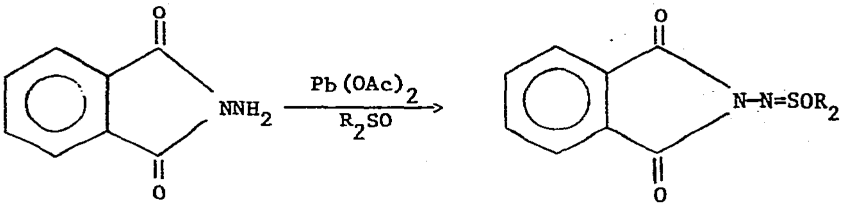
$$Ph_3AsO \xrightarrow[XNH_2]{Ac_2O} Ph_3As{=}NX$$

(where X = $MeSO_2$, $PhSO_2$, *p*-$MeC_6H_4SO_2$, PhCO, *p*-$NO_2C_6H_4CO$, and $Ph_2P(O)$)

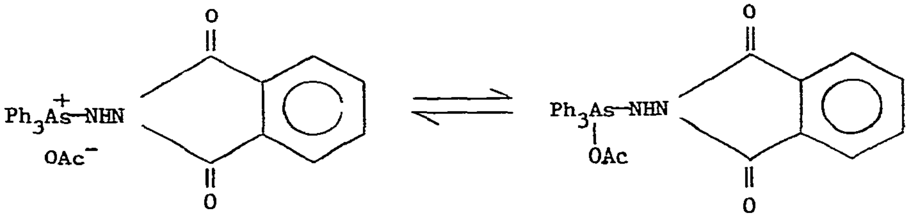
It was also demonstrated that the above reaction proceeded by two different pathways:



Finally the authors studied the reaction of Ph_3As and $Pb(OAc)_4$ with N-aminophthalimide. Again it had been previously postulated that the phthalimide was oxidized by $Pb(OAc)_4$ to nitrenes which subsequently reacted with sulphoxides to give sulfoximides:

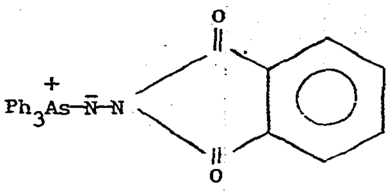


It was found the phthalimide reacted with Ph_3As and $Pb(OAc)_4$ to form the interesting aminoarsonium acetate LXII, which existed in ionic and covalent forms:



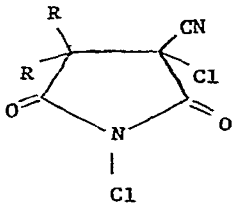
LXII

The compound LXII was hydrolysed to Ph_3AsO and N-aminophthalimide. It could also be formed by the reaction of $Ph_3As(OAc)_2$ with N-aminophthalimide. In contrast to other amides, however, N-aminophthalimide reacted rapidly with $Pb(OAc)_4$ in the absence of Ph_3As, so that there was undoubtedly more than one pathway for the formation of the product LXII. An attempt was also made to isolate the intermediate arsinimine LXIII which undoubtedly was formed. This compound, however, proved to be too hydrolytically unstable to be isolated and characterized.



LXIII

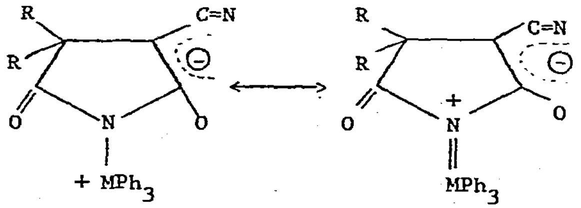
In a continuation of previous studies of the reaction of 2,5-pyrollidinediones with R_3M (M = P, As, or Sb), Leguern and coworkers [274] have investigated the reaction of Ph_3M (M = P, As, or Sb) with LXIV (R = Ph or CH_2Ph).



LXIV

(where R = Ph or $PhCH_2$)

The resulting compounds were found to be betaines with the resonant structure LXV.



LXV

A mechanism for the formation of these compounds based on the reaction of LXIV with Ph_3P was suggested. Further reactions of the phosphorus compound were also investigated. IR data on the phosphonium, arsonium, and stibonium betaines were given.

In a paper devoted to the crystal structure of $[Ph_4P][CuCl_3]$ the isomorphous $[Ph_4As][CuCl_3]$ was also investigated [275]. All dimensions for this compound were given. The preparation and IR spectrum of the arsonium salt $[Ph_4As][Re(CO)_4(NO_3)_2]$ have been described by Addison and coworkers [276]. Assignments of various bands in the IR spectra were made. An *Inorganic Syntheses* preparation [277] described salts of $[UX_6]^{2-}$ including $[Ph_4As]_2[UCl_6]$. The crystalline compound was obtained in a yield of 85% and the purity relative to U(IV) was checked by absorption spectroscopy. The IR and Raman spectra of some anionic complexes of the type $[M(CNO)_4]^{2-}$, where M = Ni, Pd, Pt, Zn, Cd and Hg, have been reported [278]. Among the cations was $[Ph_4As]^+$. The anion $[Mn_3(CO)_{14}]^-$ has been isolated as its $[Ph_4As]^+$ salt [279]. Among a series of anionic ruthenium complexes the tetraphenylarsonium compound $[Ph_4As][RuCl_3(CS)(PPh_3)]\cdot 2\ Me_2CO$ was prepared and characterized [280]. IR and NMR spectra were reported. A number of tetraphenylarsonium salts of platinum and palladium xanthates have been reported by Cornock and coworkers [281]. Examples of such compounds included $[Ph_4As][Pt(S_2COEt)_3]$ and $[Ph_4As][Pd(S_2CO)(S_2COEt)]$.

An ESR study of the tetraphenylarsonium salt $[Ph_4As]_3[RuY_3]$, where Y was the 1,1-dicyanoethylene-2,2-dithiolate grouping, has been made by Kirmse and coworkers [282]. In the course of isolating several compounds containing the ions $[Ph_2SbCl_3Y]^-$, where Y was a halogen or pseudohalogen, Bertazzi and coworkers [283] obtained the arsonium salt $[Ph_4As][Ph_2SbCl_3NCS]$. This work is described in greater detail under Antimony.

An X-ray structure determination of the tetraphenylarsonium salt $[Ph_4As][UO_2Y]\cdot 6\ H_2O$ (where Y = pyridine-2,6-dicarboxylic acid) has been made by Marangoni and coworkers [284]. Bond distances and angles for the cation were given. In a second paper from the same laboratory [285], a crystal structure of the compound $[Ph_4As]_2[UY_3]\cdot 3\ H_2O$ (where Y was the same as in the previous compound) was given in a preliminary form.

The crystal structure of the arsonium salt $[Ph_4As][CuCl_3]$ was reported by Willett and Chow [286]. The geometry of the cation was determined and showed no unusual features. The As—C distances averaged 1.91 Å and the C—As—C angles varied from 107.9° to 111.7°. The ESR spectrum of this compound was discussed in a more theoretical paper by the same authors [287]. The magnetic susceptibility of this same compound was the subject of a third paper [288].

In two papers devoted to thiocyanato and cyanato complexes of cobalt [289] and nickel [290], the arsonium salts $[Ph_4As]_2[CoN(CN)_2(NCS)_3]$, $[Ph_4As][Ni(N(CN)_2)_3]$, and $[Ph_4As]_2[NiN(CN)_2(NCS)_2]$ were prepared. IR, UV, and magnetic measurements were reported.

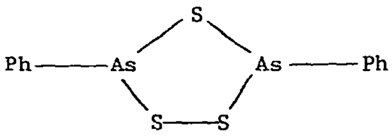
One tetraphenylarsonium salt was included in an ESR study of copper(II) maleonitriledithiolate anions [291]. Several $[R_4As]^+$ salts were included in a study of the excitation and emission spectra of compounds of the type $[R_4M]_2[MnX_4]$, where M was N, P, or As, R was an alkyl group, and X was Cl, Br, or I [292]. The preparation and spectral properties of the arsonium salts $[Ph_4As][Pd(HN{-}C{\equiv}N)_4]$ and $[Ph_4As][Pd(PhN{-}C{\equiv}N)_4]$ were described in an article by Beck and coworkers [293]. In a paper devoted to copper(I) trithiocarbonates the arsonium salt $[Ph_4As][CuCS_3]$ was described and its IR spectrum was given [294]. The vibrational spectroscopy of the arsonium salts $[Ph_4As][Ni(WO_2S_2)_2]$ and $[Ph_4As]_2[Co(WO_2S_2)_2]$ as well as several phosphonium salts has been investigated [295]. The emphasis was on the anion rather than on the cations. The ^{99}Ru Mössbauer spectra of several compounds including $[Ph_4As][RuNBr_4]$ have been described by Gibb and coworkers [296]. In a paper on organothallium thiocyanates the IR spectrum of the compound $[Ph_4As][Me_2Tl(CNS)_2]$ was discussed [297]. A gravimetric method for the determination of uranyl ions was based on the precipitation of the complex $[UO_2L_2][Ph_4As]\cdot 2\ H_2O$, where H_2L was 2,6-picolinic acid [298]. The use of Ph_4AsCl or Ph_4PCl in the separation of rhenium oxide ReO_4 from its ores by a flotation process has been the subject of a communication [299] and a patent [300].

The crystal and molecular structure of the compound $[Ph_4As][TeCl_4(OH)]H_2O$ has been determined by use of single-crystal X-ray analysis [301]. The dimensions of the Ph_4As^+ ion agreed well with previous crystallographic studies of this ion. The crystal structure of the complex $[Ph_4As]_2[Cu(NO_3)_4]CH_2Cl_2$ has been investigated [302], but the structure of the cation was not discussed.

In a paper devoted to weak and unstable anionic bromo and iodo complexes of transition metals Ryan [303] has described the preparation of the complex $[Ph_4As]_2[CeCl_6]$. Both $[Ph_4As]^+$ and $[Me_4N]^+$ salts of complex lead anions such as $Ph_3Pb(N_3)_2^-$ and $Ph_3Pb(N_3)(NCS)^-$ have been prepared and characterized by Bertazzi and co-workers [304]. The reaction of $Co(NH_3)_6Cl_2$ with CS_2 in an ammonia-saturated solution gave $[Co(NH_3)_6][Co(CS_3)_2]$ which reacted with Ph_4AsCl to give $[Ph_4As]_2[Co(CS_3)_2]$ [305].

10 COMPOUNDS WITH AS-S BONDS

The IR and Raman spectra of $Ph_2As_2S_3$ have been reported by Volka and coworkers [306] and assignments of the various bands have been made. The molecule has the structure shown in LXVI.



LXVI

G-F matrix calculations for the ring stretching vibrations were made.

In a study devoted to 3-coordinate copper complexes Tiethof and coworkers [307] have prepared the complex $[Cu(Ph_3AsS)_3]BF_4$ from Ph_3AsS and $Cu(BF_4)_2 \cdot 6\ H_2O$ in ethanol saturated with SO_2. IR data, elemental analyses, and physical properties were given for this and other similar compounds.

Complexes of the type $Me_2AsS_2Mn(CO)_4$ and $Me_2AsS_2Re(CO)_4$ have been prepared by Lindner and Ebinger [308]. The IR, Raman, and mass spectra of the complexes, as well as elementary analyses and physical properties, were given. Assignments for the principal peaks in the IR were made, and structures of the complexes were discussed in some detail. It was found that one mole of CO was lost when the complexes were warmed in a high vacuum and that an axial CO group could be replaced by a pyridine group.

Chernokal'skii and coworkers [309] have considered four different modes of attack of nucleophiles on (alkylthio)arsonium ions of the type $[R_3AsSR']^+$, and have investigated the reaction of water, alcohols, and amines on such arsonium salts. The reaction of halide ions with these arsonium salts had been investigated previously. Compounds of the type $[R_3AsSR']^+$ where R was aliphatic were stable to hydrolysis and alcoholysis. Triphenyl salts, on the other hand, gave 70–90% Ph_3As which indicated a reaction of the type:

$$[Ar_3AsSR']^+ + B \longrightarrow Ar_3As + R'SB^+$$

With $[Ph_3AsSEt][BF_4]$ and with $[Ph_3AsSMe][MeSO_4]$, the compounds $Ph_3AsO \cdot HBF_4$ and $Ph_3AsO \cdot MeHSO_4$, respectively, were isolated.

When $[Ph_3AsSEt][BF_4]$ was treated with EtOH, Ph_3AsO and $Ph_3AsO \cdot BF_3$ were isolated. Both in the reaction with H_2O and with alcohol, formation of sulfenic acid or its ester as an intermediate was postulated. The reaction of $[Ph_3AsSEt][BF_4]$ with Et_2NH gave Ph_3As and $[Et_2NH_2][BF_4]$. Similar results were obtained with Et_3N.

Chadaeva and coworkers [310] have reported on the synthesis of compounds of the type $R_nAs[S(CH_2)_mSi(OR')_3]_{3-n}$ and $R_nAs[S(CH_2)_mSiR'_3]_{3-n}$ where the R's were a variety of organic groups, mostly alkyl or aryl, *m* was 2 or 3, R' was

Me, OMe, or OEt, and n was 0, 1, or 2. Two different methods were used for the synthesis as shown by the following equations:

$$R_nAsCl_{3-n} \;+\; (3-n)HS(CH_2)_mSi(OR')_3 \longrightarrow R_nAs[S(CH_2)_m(OR')_3]_{3-n} \;+\; (3-n)HCl$$
$$R_nAs(OR'')_3 \;+\; (3-n)HS(CH_2)_mSiR'_3 \longrightarrow R_nAs[S(CH_2)_mSiR'_3]_{3-n} + (3-n)R''OH$$

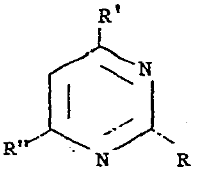
The first equation was used only for preparing the alkoxy derivatives (R = Et, Ph, and SCH_2CH_2S; R' = Me and Et) whereas by the second equation the two compounds $PhAs[S(CH_2)_3SiMe_3]_2$ and $Ph_2AsS(CH_2)_3SiMe_3$ were prepared. In the alkoxy compounds the Si–O bond was readily cleaved by water but the As–S bond remained intact. The compounds prepared possessed considerable fungicidal activity.

New alkylthioarsonium salts of the type $[R_3AsSR']X$ were prepared by Chernokal'skii and coworkers [311] by means of the following reaction:

$$R_3AsS \;+\; R'X \longrightarrow [R_3AsSR']X$$

The compounds prepared successfully were the following: R = Ph, R' = Me, X = $MeSO_4$; R = C_6H_{11}(cyclohexyl), R' = Me, X = $MeSO_4$; R = C_6H_{11}, R' = Et, X = BF_4; and R = C_6H_{11}, R' = Me, X = I.

The authors were unsuccessful in obtaining crystalline salts from (p-MeC_6H_4)$_3$AsS and Et_3AsS. In the IR and Raman spectra of the new arsonium salts, bands at 420–440 cm^{-1} were assigned to the As–S stretching vibration. Sarquis and Zingaro [312] have reported on the synthesis and spectral properties of a series of S- and Se-dimethylarsino derivatives of pyrimidines and purines. The pyrimidine compounds were prepared from the reaction of thio- or selenopyrimidines with Me_2AsNEt_2, which was prepared *in situ* from Me_2AsCl and Et_2NH. The compounds were of the type LXVII:



LXVII

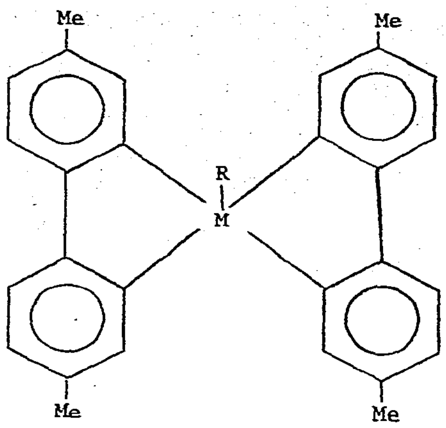
where R was $SAsMe_2$ or $SeAsMe_2$, R' was H or $SAsMe_2$, and R" was H, Me, *n*-Pr $SAsMe_2$. Elementary analyses, physical properties and ^1H NMR, IR, and mass spectra were given. The authors were unable to prepare O- or N-arsinous a derivative's from oxy- and aminopyrimidines. The dimethylarsinothio- and dimethylarsinoselenopurines were prepared by a similar procedure, except t the Me_2AsNEt was prepared and purified prior to its condensation with the appropriate thio- or selenopurine. The IR spectra of the various compound were discussed in some detail and assignments of bands were made.

In order to determine if the As=S grouping would act as the acceptor hydrogen bond formation, Shagidullin and coworkers [313] have reported on the IR spectra, the enthalpy of formation, and the association constants of a number of mixtures of phenol and various triarylarsine sulfides. The results were compared with Ph_3PS and Et_3PS, which were known to form weak hydrogen bonds with phenol, and with Ph_3AsO, all in their reactions with phenol. It was concluded that the As=S grouping in these mixtures formed more stable hydrogen bonds than the P=S grouping but less stable hydrogen bonds than the As-O grouping. A plot of IR frequency shift vs. the Kabachni σ constants for the various substituted triarylarsine sulfides gave a straig line.

11 MISCELLANEOUS

In an interesting paper by Hellwinkel and coworkers [314] the spiranes LXVIII were described.

In the case where M = P the naphthyl group was attached to P at the 1-position and in the 8-position were such groups as H, F, Cl, Br, Me, OMe, and NMe_2, and in the case of the quinolyl groups it was attached to P at the 8-position. In the case of M = As only five compounds were prepared, *viz.* the 8-quinolyl compound and the α-naphthyl, 8-fluoro, 8-chloro- and 8-Me-α-naphthyl derivatives. On the basis of ^1H and ^{31}P NMR spectra it was concluded that all of the phosphorus compounds possessed trigonal-



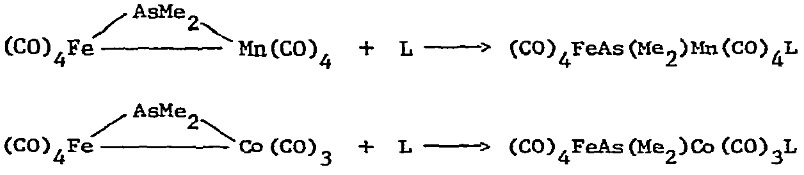
LXVIII

(where M = P or As and R = a substituted α-naphthyl or quinolyl group)

bipyramidal ground states (mainly at room temperature) and that the 8-X-1-naphthyl group (where X was one of the substitutents previously mentioned) was rigid and nearly parallel to the equatorial plane. As the temperature was raised the molecule underwent pseudoratation as well as rotation of the substituted naphthalene group. The barriers to pseudorotation $\Delta G^{\#}$ (in kcal/mole) were calculated for the different molecules and found to vary from 15.8 for the unsubstituted α-naphthyl group to ∿23.4 for the OMe group. Similar results were obtained with the arsenic compounds, but the $\Delta G^{\#}$ values were from 2-3 kcal/mole lower than for the corresponding phosphorus compounds.

An article on biological cycles for toxic elements in the environment [315] considers the reactions of various arsenic compounds which might be found in the environment. The article states that most arsenic compounds are methylated and reduced by anaerobes and the resulting toxic arsines are then oxidized to less toxic products. These, however, may in turn be reduced. Thus, cacodylic acid is an intermediate in the biosynthesis of Me_2AsH from inorganic arsenic compounds.

A group of interesting arsenicals containing arsenic-transition metal bonds has been formed by the following two cleavage reactions [316]:



$$\mathrm{(CO)_4Fe}\overset{\mathrm{AsMe_2}}{\overline{\qquad\qquad}}\mathrm{Mn(CO)_4} + \mathrm{L} \longrightarrow \mathrm{(CO)_4FeAs(Me_2)Mn(CO)_4L}$$

$$\mathrm{(CO)_4Fe}\overset{\mathrm{AsMe_2}}{\overline{\qquad\qquad}}\mathrm{Co(CO)_3} + \mathrm{L} \longrightarrow \mathrm{(CO)_4FeAs(Me_2)Co(CO)_3L}$$

(where L = $P(NMe_3)_3$, $P(OMe)_3$, PMe_2Ph, and PPh_3)

IR and NMR spectra of the compounds were discussed in considerable detail.

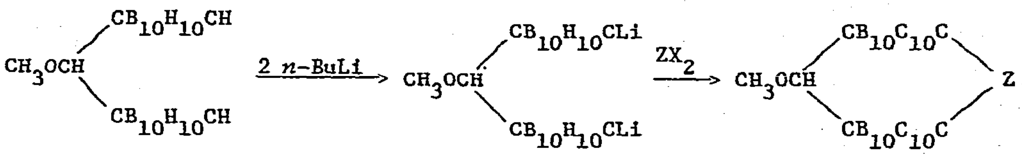
A cyclic arsenic compound containing a nine-membered arsenic ring, as revealed by X-ray analysis, has been reported by Elmes and coworkers [317]. The compound was $Cr_2(CO)_6(AsMe)_9$. The arsenic ring was puckered, and six c the nine arsenic atoms were linked to chromium. A similar compound $Mo_2(CO)_6(AsPr)_8$ contained a chain of eight arsenic atoms terminally attache to each molybdenum atom. The compounds were formed in thermal reactions between the metal carbonyls and cyclic arsines.

Although Me_3Ga reacts with Sn, Si, or Ge films at high temperatures (1 230°, and 285°, respectively) to transfer methyl groups to the films, the reaction of Me_3Ga with an arsenic film at temperatures as high as 340° fail to give any methyl arsenic compounds [318].

The preparation of the two new arsacarboranes, $B_9C_2H_{11}AsPh$ and $B_8H_8As_2$ has been reported by Siedle and Todd [319]. The mass spectra, ^1H and ^{11}B N spectra for these compounds were reported.

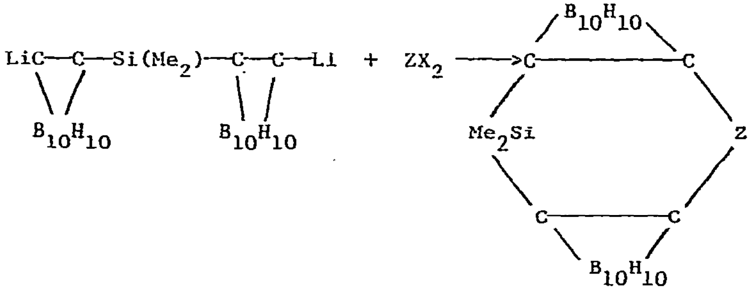
The synthesis of two new types of heteroboranes which were derived fro $7,8\text{-}C_2B_9H_{11}^{2-}$ and various organoarsenic halides has been reported by Smith an Hawthorne [320]. These compounds were of the type $RAsC_2B_9H_{11}$ (where R = Me *n*-Bu, Ph and Br) and $(R_2As)_2C_2B_9H_{11}$ (R = Me). ^{11}B NMR data were given and structures proposed for the new compounds.

Carboranes of the type LXIX were prepared by Zakharkin and Shemyakin [321] by means of the following reaction:



(where $CH_3OCH(CB_{10}H_{10}CH)_2$ was bis(o-carboranyl)methoxymethane and ZX_2 was a compound such as Me_2SiCl_2, Me_2SnCl_2, Me_2GeCl_2, $PhPCl_2$ and $MeAsI_2$)
^1H NMR data as well as elemental analyses for the new heterocyclic compounds were given.

Boron compounds of the type LXX, where Z = Me_2Sn, Me_2Ge, PhP, and MeAs, were prepared [322] by means of the following reaction:



LXX

^1H NMR data as well as elemental analyses for the new compounds were given.

It has been found [323] that the cationic complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}(cyclohexene)]^+$ and $[\pi\ C_7H_7)Mo(CO)_3]^+$ reacted with $[1,2\text{-}GeCHB_{10}H_{10}]^-$ and with arsa- and phosphaboranes to form neutral complexes. The arsa compounds used were $[7,8\text{-}B_9H_{10}As_2]^-$ and $[B_{10}H_{12}As]^-$. The arsenic compounds obtained were $(\pi\text{-}C_5H_5)Fe(CO)_2AsB_{10}H_{12}$ and $(\pi\text{-}C_5H_5)Fe(CO)_2AsB_9H_{10}$. No attempt was made to obtain a molybdenum complex of the arsaboranes. NMR spectra (^{11}B and ^1H) as well as IR data were given.

The preparation of a number of arsaboranes has been discussed in the first paper of a series devoted to Group V boranes [324]. The compound 7-$B_{10}H_{12}As^-$ was prepared by several methods; the purest product was obtained from $AsCl_3$ and decaborane in THF with Et_3N as the base and zinc dust as the reducing agent. In the presence of a twofold excess of Et_3N and excess $AsCl_3$ 1,2-$B_{10}H_{10}As_2$ was formed. 7-$B_{10}H_{12}As^-$ reacted with MeI to give $B_{10}H_{12}AsMe$. This compound readily lost a proton in dilute aqueous NH_3 to form the $[B_{10}H_{11}AsMe]^-$ ion, which could be precipitated as $[Me_4N][B_{10}H_{11}AsMe]$ The compound $B_{10}H_{12}AsPh$ was obtained from $PhAsCl_2$ and decaborane in THF in the presence of excess Et_3N. The structures proposed for these compounds were based largely on the ^{11}B NMR spectra. IR and ^1H NMR spectra were also reported.

The extraction of fluoride ion from solution with organometallic compounds of Groups IV and V as a function of pH has been discussed by Benmalek and coworkers [325]. Although a triphenylarsenic dihalide was used, it appeared to be less satisfactory than the corresponding antimony or bismuth compound.

Glucose catabolism by monomorphic *T. brucei* and pleomorphic *T. rhodesiense* and α-glutarate and pyruvate utilization by pleomorphic *T. rhodesiense* were inhibited by trivalent organic arsenic drugs [326]. Trypanasome pyruvate kinase was not inhibited by pentavalent organic arsenicals or by sodium arsenite. The drugs used were sodium melarsen, melarsen oxide, and *Mel W.*

REFERENCES

1 D. Millington, *Annu. Rep. Prog. Chem., Sect. A,* 70 (1974) 345.

2 N. N. Greenwood, Reporter, *Spectroscopic Properties of Inorganic and Organometallic Compounds,* 7 (1974).

3 O. Kennard, D. G. Watson, and W. G. Town, *Molecular Structures and Dimensions*, Vol. 5, Oosthoek, Utrecht, 1974, pp. 226, 348-363.

4 J. E. Fergusson, *Stereochemistry and Bonding in Inorganic Chemistry*, Prentice-Hall, Englewood Cliffs, N. J., 1974.

5 I. N. Azerbaev, Z. A. Abramova, and Yu. G. Bosyakov, *Usp. Khim.*, 43 (1974) 1384.

6 M. B. Hursthouse, *Mol. Struct. Diffr. Methods*, 1 (1973) 756.

7 V. I. Tel'noi, *Tr. Khim. Khim. Tekhnol.*, (1974) 28.

8 V. A. Maslova and I. B. Rabinovich, *Tr. Khim. Khim. Tekhnol.*, (1974) 40.

9 J. S. Thayer, *J. Organometal. Chem.*, 76 (1974) 265.

10 G. O. Doak and L. D. Freedman, *Synthesis*, (1974) 328.

11 E. Maslowsky, Jr., *J. Organometal. Chem.*, 70 (1974) 153.

12 A. Singh, V. D. Gupta, G. Srivastava, and R. C. Mehrotra, *J. Organometal. Chem.*, 64 (1974) 145.

13 H. C. Clark, *J. Organometal. Chem.*, 80 (1974) 155.

14 L. C. Duncan, *Annu. Rep. Inorg. Gen. Syn.* 1 (1973) 225.

15 R. E. Banks, *Fluorocarbon Relat. Chem.*, 2 (1974) 178.

16 C. S. Kraihanzel, *J. Organometal. Chem.*, 73 (1974) 137.

17 R. Morassi, I. Bertini, and L. Sacconi, *Coord. Chem. Rev.*, 11 (1973) 343.

18 B. C. Pant, *J. Organometal. Chem.*, 66 (1974) 321.

19 L. J. Todd and J. R. Wilkinson, *J. Organometal. Chem.*, 77 (1974) 1.

20 A. Tzschach and P. Franke, *J. Organometal. Chem.*, 81 (1974) 187.

21 R. B. King and A. Efraty, *J. Chem. Soc., Perkin Trans. 1*, (1974) 1371.

22 J. E. Byrne and C. R. Russ, *J. Inorg. Nucl. Chem.*, 36 (1974) 35.

23 S. Hilpert and F. Herrmann, *Ber.*, 46 (1913) 2218.

24 M. Cartwright and A. A. Woolf, *J. Inorg. Nucl. Chem.*, 36 (1974) 3858.

25 J. Ellermann and H. Schössner, *Angew. Chem., Int. Ed. Engl.*, 13 (1974) 601.

26 A. Tzschach and K. Kellner, *J. Prakt. Chem.*, 316 (1974) 851.

27 Yu. F. Gatilov, F. D. Yambushev, and N. Kh. Tenisheva, *Zh. Obshch. Khim.*, 43 (1973) 2273.

28 Yu. F. Gatilov, F. D. Yambushev, and N. Kh. Tenisheva, *Zh. Obshch. Khim.*, 43 (1973) 2681.

29 F. D. Yambushev, Yu. F. Gatilov, N. Kh. Tenisheva, and V. I. Savin, *Zh. Obshch. Khim.*, 44 (1974) 1730.

30 F. D. Yambushev, Yu. F. Gatilov, N. Kh. Tenisheva, and V. I. Savin, *Zh. Obshch. Khim.*, 44 (1974) 1734.

31 F. D. Yambushev, Yu. F. Gatilov, N. Kh. Tenisheva, and V. I. Savin, *Zh. Obshch. Khim.*, 44 (1974) 2205.

32 F. D. Yambushev, Yu. F. Gatilov, N. Kh. Tenisheva, and V. I. Savin, *Zh. Obshch. Khim.*, 44 (1974) 2499.

33 R. G. Miftakhova, I. B. Abalonia, B. D. Chernokal'skii, B. N. Laskorin, and L. A. Fedorova, *Khim. Tekhnol. Elementoorg. Soedin. Polim.*, (1972) 7; *Chem. Abstr.*, 81 (1974) 49765q.

34 W. R. Cullen and J. T. Price, *Can. J. Chem.*, 52 (1974) 1108.

35 I. N. Azerbaev, Z. A. Abramova, and Yu. G. Bosyakov (Institute of Chemical Sciences, Academy of Sciences, Kazakh SSR), U.S.S.R. Patent 423,805; *Chem. Abstra.*, 81 (1974) 4072v.

36 G. Märkl, J. Advena, and H. Hauptmann, *Tetrahedron Lett.*, (1974) 203.

37 G. Märkl, J. Advena, and H. Hauptmann, *Tetrahedron Lett.*, (1974) 303.

38 A. Tzschach and W. Voigtländer, East Ger. Pat. 99, 169; *Chem. Abstr.*, 80 (1974) 121113z.

39 A. Tzschach, D. Drohne, and J. Heinicke, East Ger. Pat. 99, 803; *Chem. Abstr.*, 80 (1974) 83244h.

40 S. T. Chow and C. A. McAuliffe, *J. Organometal. Chem.*, 77 (1974) 401.

41 Y. Matsumura, M. Harakawa, and R. Okawara, *J. Organometal. Chem.*, 71 (1974) 403.

42 M. Durand and J.-P. Laurent, *J. Chim. Phys. Physiochim. Biol.*, 71 (1974) 847.

43 D. B. Patterson and A. Carnevale, *J. Chem. Phys.*, 59 (1973) 6464.

44 G. P. Van der Kelen and R. F. de Ketelaere, *J. Mol. Struct.* 23 (1974) 329.

45 G. Kordosky, G. S. Benner, and D. W. Meek, *Inorg. Chim. Acta*, 7 (1973) 605.

46 R. R. Shagidullin, A. V. Chernova, B. D. Chernokal'skii, V. I. Gavrilov, and G. R. Gavrilova, *Khim. Geterotsikl. Soedin*, (1974) 768; *Chem. Abstr.* 82 (1975) 3527f.

47 S. Elbel, H. Bergmann, and W. Ensslin, *J. Chem. Soc., Faraday Trans.* 2, 70 (1974) 555.

48 T. P. Debies and J. W. Rabalais, *Inorg. Chem.*, 13 (1974) 308.

49 U. Kh. Rasulev, É. Ya. Zandberg, and G. M. Bogolyubov, *Zh. Obshch. Khim.*, 44 (1974) 2198.

50 V. K. Potapov, A. N. Rodionov, T. I. Evlasheva, and K. L. Rogozhin, *Khim. Vys. Energ.*, 8 (1974) 559; *Chem. Abstr.*, 82 (1975) 57009g.

51 R. F. De Ketelaere and G. P. Van der Kelen, *J. Organometal. Chem.*, 73 (1974) 251.

52 B. Bosnich, W. G. Jackson, and S. B. Wild, *Inorg. Chem.*, 13 (1974) 1121.

53 B. Bosnich, W. G. Jackson, and J. W. McLaren, *Inorg. Chem.*, 13 (1974) 1133.

54 W. R. Cullen, L. D. Hall, J. T. Price and G. Spendjian, *J. Amer. Chem. Soc.*, 96 (1974) 410.

55 W. R. Cullen, L. D. Hall, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 96 (1974) 3422.

56 W. R. Cullen, L. D. Hall, H. K. Spendjian, and J. E. H. Ward, *J. Fluorine Chem.*, 3 (1974) 341.

57 W. R. Cullen, L. D. Hall, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 96 (1974) 3431.

58 J. R. Durig, B. A. Hudgens, and J. D. Odom, *Inorg. Chem.*, 13 (1974) 2306.

59 M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem.*, 36 (1974) 2175.

60 S. S. Sandhu and G. S. Aulakh, *Proc. Chem. Symp.*, 2 (1972) 169; *Chem. Abstr.*, 81 (1974) 180493s.

61 K. A. Dari and J. V. Kingston, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 1087.

62 D. Rehder and J. Schmidt, *J. Inorg. Nucl.Chem.*, 36 (1974) 333.

63 C. A. McAuliffe and D. G. Watson, *J. Chem. Soc., Dalton Trans.*, (1974) 1531.

64 W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 11 (1974) 33.

65 T. N. Lockyer, *Aust. J. Chem.*, 27 (1974) 259.

66 G. M. Intille (Monsanto Co.), U. S. Pat. 3,796,739; *Chem. Abstr.*, 80 (1974 121117d.

67 J. A. Bowden, R. Colton, and Z. Sztajer, *Aust. J. Chem.*, 27 (1974) 401.

68 W. Hewertson and H. R. Watson, *J. Chem. Soc.* (1962) 1490.

69 F. A. Cotton and T. R. Webb, *Inorg. Chim. Acta*, 10 (1974) 127.

70 R. G. Hayter, *Inorg. Chem.*, 3 (1964) 711.

71 W. Malisch and M. Kuhn, *Angew. Chem., Int. Ed. Engl.*, 13 (1974) 84.

72 C. A. McAuliffe and R. Pollock, *J. Organometal. Chem.*, 74 (1974) 463.

73 K. Suzuki, H. Yamamoto, and S. Kanie, *J. Organometal. Chem.*, 73 (1974) 131.

74 F. T. Delbeke and G. P. Van der Kelen, *J. Organometal Chem.*, 64 (1974) 239.

75 G. B. Robertson and P. O. Whimp, *Inorg. Chem.*, 13 (1974) 1047.

76 S. S. Sandhu and A. K. Mehta, *J. Organometal. Chem.*, 77 (1974) 45.

77 S. C. Tripathi, S. C. Srivastava, and A. K. Shrimal, *J. Organometal. Chem.*, 73 (1974) 343.

78 T. Fukumoto, Y. Matsumura, and R. Okawara, *J. Organometal. Chem.*, 69 (1974) 437.

79 B. Bosnich, W. G. Jackson and S. T. D. Lo, *Inorg. Chem.*, 13 (1974) 2598.

80 B. Bosnich, W. G. Jackson, S. T. D. Lo and J. W. McLaren, *Inorg. Chem.*, 13 (1974) 2605.

81 D. J. Thornhill and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, (1974) 6.

82 G. Innorta, S. Torroni, and A. Foffani, *J. Organometal. Chem.*, 66 (1974) 459.

83 D. Negoiu, C. Pârlog, and D. Sândulescu, *Rev. Roum. Chim.*, 19 (1974) 387.

84 A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Zh. Obshch. Khim.*, 44 (1974) 1079.

85 R. T. Sane and P. R. Kulkarni, *Curr. Sci.*, 43 (1974) 42; *Chem. Abstr.*, 80 (1974) 77801w.

86 E. Uhlig and B. Machelett, *Z. Anorg. Allg. Chem.*, 409 (1974) 320.

87 M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 13 (1974) 1899.

88 A. G. Jones and D. B. Powell, *Spectrochim. Acta, Part A*, 30 (1974) 563.

89 G. van Koten and J. G. Noltes, *J. Organometal. Chem.*, 80 (1974) C56.

90 R. Usón, P. Royo, and A. Laguna, *J. Organometal. Chem.*, 69 (1974) 361.

91 M. A. Bennett and T. R. B. Mitchell, *J. Organometal. Chem.*, 70 (1974) C30.

92 P. R. Brookes and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1974) 1702.

93 R. Brady, W. V. Miller, and L. Vaska, *J. Chem. Soc., Chem. Commun.*, (1974) 393.

94 D. G. E. Kerfoot, R. J. Mawby, A. Sgamellotti, and L. M. Venanzi, *Inorg. Chim. Acta*, 8 (1974) 195.

95 G. K. N. Reddy and N. M. N. Gowda, *Indian J. Chem.*, 12 (1974) 185.

96 R. J. Mynott, E. F. Trogu, and L. M. Venanzi, *Inorg. Chim. Acta*, 8 (1974) 201.

97 C. A. McAuliffe and R. Pollock, *J. Organometal. Chem.*, 69 (1974) C13.

98 B. R. Rao, M. R. Hussain, G. K. N. Reddy, and E. G. Leelamani, *Curr. Sci.*, 43 (1974) 325.

99 G. K. N. Reddy and E. G. Leelamani, *J. Inorg. Nucl. Chem.*, 36 (1974) 295.

100 R. K. Poddar and U. Agarwala, *J. Inorg. Nucl. Chem.*, 36 (1974) 575.

101 H. L. Conder and M. Y. Darensbourg, *J. Organometal. Chem.*, 67 (1974) 93.

102 R. Edwards, J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1974) 2105.

103 G. Cardaci, *Inorg. Chem.*, 13 (1974) 368.

104 W. T. Oosterhuis, D. L. Weaver and E. A. Paez, *J. Chem. Phys.*, 60 (1974) 1018.

105 M. Herberhold and A. Razavi, *J. Organometal. Chem.*, 67 (1974) 81.

106 J. A. Connor and G. A. Hudson, *J. Organometal. Chem.*, 73 (1974) 351.

107 N. J. Coville and I. S. Butler, *J. Organometal. Chem.*, 64 (1974) 101.

108 W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, *Inorg. Chem.*, 13 (1974) 2130.

109 W. R. Cullen, L. Mihichuk, F. W. B. Einstein, and J S. Field, *J. Organometal. Chem.*, 73 (1974) C53.

110 M. G. B. Drew, G. M. Egginton, and J. D. Wikins, *Acta Cryst., Sect. B*, 30 (1974) 1895.

111 A. Harris and A. J. Rest, *J. Organometal. Chem.*, 78 (1974) C29.

112 C. D. Hem, M. Dartiguenave, and Y. Dartiguenave, *Inorg. Nucl. Chem. Lett.* 10 (1974) 1039.

113 P. Dapporto and L. Sacconi, *Inorg. Chim. Acta*, 9 (1974) L2

114 C. A. McAuliffe and D. G. Watson, *J. Organometal. Chem.*, 78 (1974) C51.

115 F. T. Delbeke, G. P. Van der Kelen, and Z, Eeckhout, *J. Organometal. Chem.*, 64 (1974) 265.

116 J. W. Buchler and K. Rohbock, *J. Organometal. Chem.*, 65 (1974) 223.

117 D. Pawson and W. P. Griffith, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 253.

118 W. Beck, K. Schorpp, and C. Oetker, *Chem. Ber.*, 107 (1974) 1380.

119 W. Levason and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, (1974) 2238.

120 J. M. Duff, B. E. Mann, B. L. Shaw, and B. Turtle, *J. Chem. Soc., Dalton Trans.*, (1974) 139.

121 N. M. N. Gowda and G. K. N. Reddy, *Aust. J. Chem.*, 27 (1974) 2557.

122 E. Ban, R. P. Hughes, and J. Powell, *J. Organometal. Chem.*, 69 (1974) 455.

123 P. L. Goggin and J. Mink, *J. Chem. Soc., Dalton Trans.*, (1974) 534.

124 E. Uhlig and S. Keiser, *Z. Anorg. Allg. Chem.*, 406 (1974) 1.

125 G. M. Bancroft and K. D. Butler, *J. Amer. Chem. Soc.*, 96 (1974) 7208.

126 T. G. Appleton, H. C. Clark, and L. E. Manzer, *J. Organometal. Chem.*, 65 (1975) 275.

127 D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *J. Organometal. Chem.*, 72 (1974) 139.

128 W. J. Cherwinski, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1974) 1405.

129 R. L. Hassel and J. L. Burmeister, *Inorg. Chim. Acta*, 8 (1974) 155.

130 R. Usón, P. Royo, and J. Gimeno, *J. Organometal. Chem.*, 72 (1974) 299.

131 J. F. Van Baar, K. Vrieze, and D. J. Stufkens, *J. Organometal. Chem.*, 81 (1974) 247.

132 C. J. Wilson, M. Green and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, (1974) 1293.

133 H. C. Clark and J. E. H. Ward, *Can. J. Chem.*, 52 (1974) 570.

134 H. C. Clark and J. E. H. Ward, *J. Am. Chem. Soc.*, 96 (1974) 1741.

135 H. C. Clark, L. E. Manzer, and J. E. H. Ward, *Can. J. Chem.*, 52 (1974) 1165.

136 J. Dehand and J. F. Nennig, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 875.

137 C. J. Wilson, M. Green and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, (1974) 421.

138 P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, (1974) 523.

139 H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 81 (1974) C31.

140 P. K. Maples, M. Green, F. G. A. Stone and J. L. Spencer, *J. Chem. Soc., Dalton Trans.*, (1974) 1194.

141 M. Lenarda, R. Ros, M. Graziani, and U. Belluco, *J. Organometal. Chem.*, 65 (1974) 407.

142 R. Schlodder, J. A. Ibers, M. Lenarda, and M. Graziani, *J. Am. Chem., Soc.*, 96 (1974) 6893.

142a A. G. Maddock and A. Pires de Matos, *Radiochim. Acta,* 19 (1973) 163.

143 C. C. Addison, R. Davis, and N. Logan, *J. Chem. Soc., Dalton Trans.*, (1974) 2070.

144 D. J. Darensbourg and D. Madrid, *Inorg. Chem.*, 13 (1974) 1532.

145 E. Lindner and H. Berke, *J. Organometal. Chem.*, 72 (1974) 197.

146 E. M. Maslen, J. C. Dewan, D. L. Kepert, K. R. Trigwell and A. H. White, *J. Chem. Soc., Dalton Trans.*, (1974) 2128.

147 P. E. Garrou and G. E. Hartwell, *J. Chem. Soc., Chem. Commun.*, (1974) 381.

148 A. C. Jarvis and R. D. W. Kemmitt, *J. Organometal. Chem.*, 81 (1974) 415.

149 M. Nonoyama, *J. Organometal. Chem.*, 74 (1974) 115.

150 K. Goswami and M. M. Singh, *Indian J. Chem.*, 12 (1974) 858.

151 A. Peloso and L. Volponi, *J. Chem. Soc., Dalton Trans.*, (1974) 278.

152 G. K. N. Reddy and B. R. Ramesh, *Proc. Chem. Symp.*, 2 (1972) 143; *Chem. Abstr.*, 81 (1974) 180497w.

153 G. K. N. Reddy and B. R. Ramesh, *J. Organometal. Chem.*, 67 (1974) 443.

154 M. A. Bennett, R. N. Johnson and I. B. Tomkins, *Inorg. Chem.*, 13 (1974) 346.

155 A. Poë and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, (1974) 1860.

156 R. K. Poddar, U. Agarwala, and P. T. Manoharan, *J. Inorg. Nucl. Chem.*, 36 (1974) 2275.

157 M. M. T. Khan and R. K. Andal, *Proc. Chem. Symp.*, 2 (1972) 133; *Chem. Abstr.*, 81 (1974) 180499y.

158 M. M. T. Khan and S. Vancheesan, *Proc. Chem. Symp.*, 2 (1972) 137; *Chem. Abstr.*, 81 (1974) 180498x.

159 L. Ruiz-Ramírez and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, (1974) 1640.

160 S. S. Sandhu and A.K.Mehta, *Indian J. Chem.*, 12 (1974) 834.

161 M. K. Cooper, R. S. Nyholm, P. W. Carreck, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, (1974) 343.

162 W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 8 (1974) 25.

163 H. Nakayama, C. Nishijima, and S. Tachiyashiki, *Chem. Lett.*, (1974) 733.

164 R. P. Stewart, Jr., *J. Organometal. Chem.*, 70 (1974) C8.

165 M. G. B. Drew and J. D. Wilkins, *J. Organometal. Chem.*, 69 (1974) 271.

166 A. Mercer and J. Trotter, *Can. J. Chem.*, 52 (1974) 3331.

167 D. Rehder and J. Schmidt, *J. Inorg. Nucl. Chem.*, 36 (1974) 333.

168 S. S. Pahil and K. D. Sharma, *Fresenius Z. Anal. Chem.*, 270 (1974) 127.

169 M. J. Bevan and D. Husain, *J. Photochem.*, 3 (1974) 1; *Chem. Abstr.*, 81 (1974) 161631u.

170 O. M. Nefedov, S. P. Kolesnikov, and I. S. Rogozhin, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1973) 2824.

171 V. A. Maslova, V. P. Nistratov, and I. B. Rabinovich, *Tr. Khim. Khim. Tekhnol.*, (1973) 53; *Chem. Abstr.*, 80 (1974) 95061j.

172 E. I. Leupold and H. J. Arpe (Farbwerke Hoechst A.-G.), Ger. Offen. 2, 252, 514; *Chem. Abstr.*, 81 (1974) 25101u.

173 V. N. Fedorenko, Yu. A. Rainov, E. B. Sokolov, B. T. Gribov, A. T. Akhin'ko and B. I. Kozyrkin, *Sb. Nauch. Tr. Probl. Mikroelektron., Mosk. Inst. Elektron. Tekh.*, (1972) 152; *Chem. Abstr.*, 80 (1974) 133527a.

174 J. Ellermann, H. Schössner, A. Haag, and H. Schödel, *J. Organometal. Chem.*, 65 (1974) 33.

175 R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, 96 (1974) 112.

176 H. G. Ang and W. S. Lien, *J. Fluorine Chem.*, 4 (1974) 447.

177 J. Kaufmann and F. Kober, *J. Organometal. Chem.*, 71 (1974) 49.

178 J. Kaufmann and F. Kober, *J. Organometal. Chem.*, 81 (1974) 59.

179 F. Kober and W. J. Rühl, *Z. Anorg. Allg. Chem.*, 406 (1974) 52.

180 F. Kober, *Z. Naturforsch.*, *Teil B*, 29 (1974) 358.

181 O. Adler and F. Kober, *J. Organometal. Chem.*, 72 (1974) 351.

182 R. D. Gigauri, M. A. Indzhiya, B. D. Chernokal'skii, M. M. Ugulava, and Ts. A. Sidamashvili, *Zh. Obshch. Khim.*, 44 (1974) 1541.

183 R. D. Gigauri, G. N. Chachava, B. D. Chernokal'skii, and M. M. Ugulava, *Zh. Obshch. Khim.*, 44 (1974) 1720.

184 G. N. Birich, G. I. Drozd, V. N. Sorokin, and I. I. Struk, *Pis'ma Zh. Eksp. Teor. Fiz.*, 19 (1974) 44; *Chem. Abstr.*, 80 (1974) 102117n.

185 D. Valigura, G. Ondrejovič, D. Makáňová, and J. Gažo, *Chem. Zvesti.*, 28 (1974) 599.

186 D. Makáňová, G. Ondrejovič, D. Valigura, and J. Gažo, *Chem. Zvesti.*, 28 (1974) 604.

187 P. Jutzi and M. Kuhn, *Chem. Ber.*, 107 (1974) 1228.

188 G. Saint-Ruf, J.-C. Perche, and D. P. Hien, *Bull. Soc. Chim. Fr.*, (1974) 521.

189 I. P. Biryukov and A. Ya. Deich, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* (1974) 285; *Chem. Abstr.*, 81 (1974) 119751h.

190 S. C. Pace and J. G. Riess, *J. Organometal. Chem.*, 76 (1974) 325.

191 A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Amer. Chem. Soc.*, 96 (1974) 2648.

192 G. Fritz, H. Schäfer, R. Demuth, and J. Grobe, *Z. Anorg. Allg. Chem.*, 407 (1974) 287.

193 K. Henrick, D. L. Kepert, E. Shewchuk, K. R. Trigwell, and S. B. Wild, *Aust. J. Chem.*, 27 (1974) 727.

194 D. T. Clark and I. W. Scanlan, *J. Chem. Soc., Faraday Trans. 2*, 70 (1974) 1222.

195 Yu. F. Gatilov, L. B. Ionov, A. P. Korovyakov, and L. G. Kokorina, *Zh. Obshch. Khim.*, 43 (1973) 2677.

196 Yu. F. Gatilov, L. B. Ionov, L. G. Kokorina, and I. P. Mukanov, *Zh. Obshch. Khim.*, 44 (1974) 1727.

197 L. B. Ionov, Yu. F. Gatilov, I. P. Mukanov, and L. G. Kokorina, *Zh. Obshch. Khim.*, 44 (1974) 1737.

198 L. B. Ionov, Yu. F. Gatilov, I. P. Mukanov, and L. G. Kokorina, *Zh. Obshch. Khim.*, 44 (1974) 1874.

199 R. G. Kostyanovskii, Yu. I. Él'natanov, K. S. Zakharov, and L. M. Zagurskaya, *Dokl. Akad. Nauk SSSR*, 219 (1974) 137.

200 F. M. Khusnutdinova, V. I. Gavrilov, and B. D. Chernokal'skii, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 17 (1974) 147; *Chem. Abstr.*, 80 (1974) 96109t.

201 G. Märkl and C. Martin, *Tetrahedron Lett.*, (1973) 4503.

202 G. Märkl, H. Baier, and C. Martin, *Tetrahedron Lett.*, (1974) 1977.

203 G. Märkl and F. Kneidl, *Angew. Chem., Int. Ed. Engl.*, 12 (1973) 931.

204 G. Märkl and F. Kneidl, *Angew. Chem., Int. Ed. Engl.*, 13 (1974) 667.

205 G. Märkl and F. Kneidl, *Angew. Chem., Int. Ed. Engl.*, 13 (1974) 668.

206 T. J. Bastow and P. S. Elmes, *Aust. J. Chem.*, 27 (1974) 413.

207 M. Durand and J.-P. Laurent, *J. Organometal. Chem.*, 77 (1974) 225.

208 P. J. Busse, K. J. Irgolic, and R. J. G. Dominguez, *J. Organometal. Chem.*, 81 (1974) 45.

209 F. K Vansant and B. J. Van der Veken, *J. Mol. Struct.*, 22 (1974) 273.

210 A. Chatterjee and S. P. Sen Gupta, *Indian J. Phys.*, 48 (1974) 856.

211 A. S. Selivanova, Zh. V. Molodykh, V. S. Gamayurova, B. D. Chernokal'skii, and S. V. Il'ina, *Dokl. Acad. Nauk SSSR*, 218 (1974) 493.

212 B. D. Chernokal'skii and V. A. Valiullina, *Khim. Tekhnol. Elementoorg. Soedin. Polim.*, (1972) 91; *Chem. Abstr.*, 81 (1974) 168856e.

213 B. D. Chernokal'skii, V. A. Valiullina, R. R. Shagidullin, and L. V. Avvakumova, *Zh. Obshch. Khim.*, 44 (1974) 1722.

214 V. S. Gamayurova, B. D. Chernokal'skii, A. S. Selivanova, Zh. V. Molodykh, and I. N. Zykov (Kazan Veterinary Institute and Kazan Chemical-

Technological Institute),U.S.S.R. Pat.436, 824; *Chem. Abstr.*, 81 (1974) 152419d.

215 M. Zenki, *Bunseki Kagaku*, 22 (1973) 1013; *Chem. Abstr.*, 80 (1974) 77919r.

216 S. S. Sandhu and G. K. Sandhu, *Indian J. Chem.*, 12 (1974) 830.

217 S. S. Sandhu, J. Kaur, and G. K. Sandhu, *Syn. React. Inorg. Metal-Org. Chem.*, 4 (1974) 437.

218 A. A. Abou Ouof, M. A. El-Dawy, and S. R. El-Shabouri, *Egypt. J. Pharm. Sci.*, 13 (1972) 237; *Chem. Abstr.*, 82 (1975) 57831u.

219 H.-V. Gründler, H.-D. Schumann, and E. Steger, *J. Mol. Struct.* 21 (1974) 149.

220 F. K. Vansant, B. J. van der Veken, and M. A. Herman, *Spectrochim. Acta, Part A*, 30 (1974) 69.

221 A. V. Ilyasov, Ya. A. Levin, and I. D. Morosova, *J. Mol. Struct.*, 19 (1973) 671.

222 V. S. Gamayurora, Z. G. Daineko, B. D. Chernokal'skii, R. R. Shagidullin, I. A. Lamanova, and L. V. Avvakumova, *Zh. Obshch. Khim.*, 44 (1974) 1537.

223 D. R. Wise, W. J. Hartley, and N. G. Fowler, *Res. Vet. Sci.*, 16 (1974) 336; *Chem. Abstr.*, 82 (1975) 11828v.

224 R. R. Carlson and D. W. Meek, *Inorg. Chem.*, 13 (1974) 1741.

225 R. Bravo, M. Durand, J.-P. Laurent, and F. Gallais, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 278 (1974) 1489.

226 R. B. King and P. R. Heckley, *Phosphorus*, 3 (1974) 209.

227 D. Jannakoudakis, P. G. Mavridis, and N. Missaelidis, *Epistem. Epeteris Sch. Phys. Math. Epistem., Aristoteleion Panepistem. Thessalonikes*, 13 (1973) 97; *Chem. Abstr.*, 80 (1974) 103198b.

228 D. K. Padma, R. A. Shaw, A. R. V. Murthy, and M. Woods, *Phosphorus*, 4 (1974) 25.

229 R. R. Shagidullin, *Advan. Mol. Relaxation Processes*, 5 (1973) 157.

230 B. Plesničar, R. Kavčič, and D. Hadži, *J. Mol. Struct.*, 20 (1974) 457.

231 S. Milićev, *Spectrochim. Acta, Part A,* 30 (1974) 255.

232 S. Zecchin, G. Schiavon, G. Cogoni,and G. Bontempelli, *J. Organometal. Chem.,* 81 (1974) 49.

233 D. Brandes and A. Blaschette, *J. Organometal. Chem.,* 73 (1974) 217.

234 A. M. Galeev, N. A. Chadaeva, A. Sh. Mukhtarov,and A. V. Il'yasov, *Zh. Strukt. Khim.,* 15 (1974) 927.

235 B. J. Brisdon and D. Cocker, *Inorg. Nucl. Chem. Lett.,* 10 (1974) 179.

236 U. Sartorelli, F. Canziani,and L. Garlaschelli, *Gazz. Chim. Ital.,* 104 (1974) 567.

237 B. N. Laskorin, V. V. Yakshin, L. A. Fedorova,and N. A. Lyubosvetova, *Dokl. Akad. Nauk SSSR,* 219 (1974) 1123; *Chem. Abstr.,* 82 (1975) 85584j.

238 R. Usón, A. Laguna,and J. L. Sanjoaquin, *J. Organometal. Chem.,* 80 (1974) 147.

239 M. Ciampolini and C. Mengozzi, *Gazz. Chim. Ital.,* 104 (1974) 1059.

240 S. Casey, W. Levason,and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* (1974) 886.

241 C. Santini-Scampucci and J. G. Riess, *J. Organometal. Chem.,* 73 (1974) C13.

242 S. Ploştinaru and P. Spacu, *Rev. Roum. Chim.,* 19 (1974) 567.

243 L. B. Ionov, Yu. F. Gatilov, I. P. Mukanov, and L. G. Kokorina, *Zh. Obshch. Khim.,* 44 (1974) 2502.

244 S. Sunder, B. Chawla,and J. C. Ahluwalia, *J. Phys. Chem.,* 78 (1974) 738.

245 B. Marticorena and M. Nechtschein, *Magn. Resonance Relat. Phenomena, Proc. Congr. AMPERE, 17th* (1973) 505; *Chem. Abstr.,* 81 (1974) 43662g.

246 F. Devreux and M. Nechtschein, *Pulsed Nucl. Magn. Resonance Spin Dyn. Solids, Proc. Spec. Colloq. Ampere, 1st* (1973) 212; *Chem. Abstr.,* 81 (1974) 18929s.

247 S. A. Fieldhouse, H. C. Starkie and M. C. R. Symons, *Chem. Phys. Lett.*, 23 (1973) 508.

248 V. M. Tsentovskii, V. P. Barabanov, R. B. Bairamov, and B. D. Chernokal'skii, *Zh. Obshch. Khim.*, 44 (1974) 2379.

249 V. M. Tsentovskii, B. D. Chernokal'skii, G. N. Chachava, R. D. Gigauri, and M. M. Ugulara, *Soobshch. Akad. Nauk Gruz. SSR*, 73 (1974) 385; *Chem. Abstr.*, 81 (1974) 17499q.

250 L. Horner, J. Röder, and D. Gammel, *Phosphorus*, 3 (1973) 175.

251 O. Glemser and R. Höfer, *Z. Naturforsch., Teil B*, 29 (1974) 121.

252 B. B. Srivastava, A. K. Dublish, and A. N. Pandey, *Z. Naturforsch., Teil A*, 29 (1974) 602.

253 M. Gouterman and P. Sayer, *J. Mol. Spectrosc.*, 53 (1974) 319.

254 H. Kunz, *Justus Liebigs Ann. Chem.*, (1973) 2001.

255 G. Vetter and G. Klar, *Z. Naturforsch., Teil B*, 28 (1973) 287.

256 G. Vetter, J. Kopf, and G. Klar, *Z. Naturforsch., Teil B*, 28 (1973) 293.

257 G. M. Semeniuk and D. B. Chesnut, *Chem. Phys. Lett.*, 25 (1974) 251.

258 J. Dahlmann and L. Austenat, *Justus Liebigs Ann. Chem.*, 729 (1969) 1.

259 B. D. Chernokal'skii, L. A. Vorob'eva, R. R. Shagidullin, I. A. Lamanova, and T. V. Zykova, *Zh. Obshch. Khim.*, 43 (1973) 2674.

260 B. E. Abalonin, Yu. F. Gatilov, and Z. M. Izmailova, *Zh. Obshch. Khim.*, 44 (1974) 149.

261 Yu. F. Gatilov, B. E. Abalonin, and Z. M. Ismailova, *Dokl. Akad. Nauk SSSR*, 216 (1974) 800.

262 Yu. F. Gatilov and M. G. Kralichkina, *Zh. Obshch. Khim.*, 42 (1972) 538.

263 B. E. Abalonin, Yu. F. Gatilov, and Z. M. Izmailova, *Zh. Obshch. Khim.*, 44 (1974) 1543.

264 L. Horner and S. Samaan, *Phosphorus*, 3 (1973) 153.

265 L. Horner and S. Samaan, *Phosphorus*, 4 (1974) 1.

266 W. Wolfsberger, *Z. Naturforsch., Teil B*, 29 (1974) 35.

267 H Lumbroso, D. M. Bertin, and P. Froyen, *Bull. Soc. Chim. Fr.*, (1974) 819.

268 H. Lumbroso, D. Lloyd, and G. S. Harris, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 278 (1974) 219.

269 B. H. Freeman and D. Lloyd, *Tetrahedron*, 30 (1974) 2257.

270 B. H. Freeman and D. Lloyd, *J. Chem. Soc., C*, (1971) 3164.

271 H. B. Stegmann, K. Scheffler, G. Bauer, R. Grimm, S. Hieke, and D. Stürner, *Phosphorus*, 4 (1974) 165.

272 J. I. G. Cadogan and I. Gosney, *J. Chem. Soc., Perkin Trans. 1*, (1974) 460.

273 J. I. G. Cadogan and I. Gosney, *J. Chem. Soc., Perkin Trans. 1*, (1974) 466.

274 D. Leguern, G. Morel, and A. Foucaud, *Tetrahedron Lett.*, (1974) 955.

275 M. Textor, E. Dubler, and H. R. Oswald, *Inorg. Chem.*, 13 (1974) 1361.

276 C. C. Addison, R. Davis, and N. Logan, *J. Chem. Soc., Dalton Trans.*, (1974) 1073.

277 J. L. Ryan, *Inorg. Synth.*, 15 (1974) 235.

278 W. Beck, C.-J. Oetker, and P. Swoboda, *Z. Naturforsch., Teil B*, 28 (1973) 229.

279 R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, 96 (1974) 988.

280 T. A. Stephenson, E. S. Switkes, and P. W. Armit, *J. Chem. Soc., Dalton Trans.*, (1974) 1134.

281 M. C. Cornock, D. F. Steele, and T. A. Stephenson, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 785.

282 R. Kirmse, W. Dietzsch, and E. Hoyer, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 819.

283 N. Bertazzi, L. Pellerito, and G. C. Stocco *Inorg. Nucl. Chem. Lett.*, 10 (1974) 855.

284 G. Marangoni, S. Degetto, R. Graziani, G. Bombieri, and E. Forsellini, *J. Inorg. Nucl. Chem.*, 36 (1974) 1787.

285 L. Baracco, G. Bombieri, S. Degetto, E. Forsellini, R. Graziani, and G. Marangoni, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 1045.

286 R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, 30 (1974) 207.

287 C. Chow and R. D. Willett, *J. Chem. Phys.*, 59 (1973) 5903.

288 C. Chow, R. Caputo, R. D. Willett, and B. C. Gerstein, *J. Chem. Phys.*, 61 (1974) 27

289 H. Köhler, T. P. Lischko, H. Hartung, and A. M. Golub, *Z. Anorg. Allg. Chem.*, 403 (1974) 35.

290 H. Köhler, H. Hartung, and A. M. Golub, *Z. Anorg. Allg. Chem.*, 403 (1974) 41.

291 R. Kirmse, W. Dietzsch, R. Heber, and E. Hoyer, *Z. Chem.*, 14 (1974) 26.

292 M. Wrighton and D. Ginley, *Chem. Phys.*, 4 (1974) 295; *Chem. Abstr.*, 81 (1974) 43507k.

293 W. Beck, H. Bock, and R. Schlodder, *Z. Naturforsch., Teil B*, 29 (1974) 75.

294 G. Gattow and C. W. Voigt, *Z. Anorg. Allg. Chem.*, 409 (1974) 185.

295 A. Mueller, H.-H. Heinsen, and G. Vandrish, *Inorg. Chem.*, 13 (1974) 1001.

296 T. C. Gibb, R. Greatrex, N. N. Greenwood, and R. H. Meinhold, *Chem. Phys. Lett.*, 29 (1974) 379.

297 N. Bertazzi, G. C. Stocco, L. Pellerito, and A. Silvestri, *J. Organometal. Chem.*, 81 (1974) 27.

298 L. Cattalini, S. Degetto, and G. Marangoni, *Atti Accad. Peloritana Pericolanti, Cl. Sci. Fis., Mat. Natur.*, 52 (1972) 5; *Chem. Abstr.*, 80 (1974) 152419h.

299 S. S. Semeshkin, G. A. Nelidova, and S. I. Mitrofanov, *Tsvet. Metal.*, (1974) 80; *Chem. Abstr.*, 81 (1974) 124492d.

300 S. S. Semeshkin, G. A. Nelidova, S. I. Mitrofanov, V. P. Nebera, K. F. Levin, M. A. Shevelevich, S. F. Kuz'kin, L. A. Larionov, A. T. Miroshnik, and M. N. Kasitsyn (State Scientific-Research Institute of Non-Ferrous Metals) U.S.S.R. Pat. 398,276; *Chem. Abstra.*, 81 (1974) 80921m.

301 P. H. Collins and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1974) 1545.

302 T. J. King and A. Morris, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 237.

303 J. L. Ryan, *Inorg. Synth.*, 15 (1974) 225.

304 N. Bertazzi, G. Alonzo, G. C. Stocco, and L. Pellerito, *J. Organometal. Chem.*, 80 (1974) 225.

305 A. Bruhn and H. Seidel, *Z. Naturforsch., Teil B*, 29 (1974) 123.

306 K. Volka, P. Adámek, H. Schulze, and H. J. Barber, *J. Mol. Struct.*, 21 (1974) 457.

307 J. A. Tiethof, A. T. Hetey and D. W. Meek, *Inorg. Chem.*, 13 (1974) 2505.

308 E. Lindner and H.-M. Ebinger, *J. Organometal. Chem.*, 66 (1974) 103.

309 B. D. Chernokal'skii, I. B. Levenshtein, R. R. Shagidullin, and S. V. Izosimova, *Zh. Obshch. Khim.*, 44 (1974) 2208.

310 N. A. Chadaeva, K. A. Mamakov, D. A. Iskhakova, and G. Kh. Kamai, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1974) 226.

311 B. D. Chernokal'skii, I. B. Levenshtein, R. R. Shagidullin, S. V. Izosimova, and I. A. Lamanova, *Zh. Obshch. Khim.*, 44 (1974) 1871.

312 A. M. Sarquis and R. A. Zingaro, *J. Heterocycl. Chem.*, 10 (1973) 909.

313 R. R. Shagidullin, S. V. Izosimova, and I. A. Lamanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1973) 2778.

314 D. Hellwinkel, W. Lindner, and H.-J. Wilfinger, *Chem. Ber.*, 107 (1974) 1428.

315 J. M. Wood, *Science*, 183 (1974) 1049.

316 A. Mayr, W. Ehrl, and H. Vahrenkamp, *Chem. Ber.*, 107 (1974) 3860.

317 P. S. Elmes, B. M. Gatehouse, D. J. Lloyd, and B. O. West, *J. Chem. Soc., Chem. Commun.*, (1974) 953.

318 D. J. Schlyer and M. A. Ring, *J. Organometal. Chem.*, 71 (1974) C25.

319 A. R. Siedle and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, (1973) 914.

320 H. D. Smith, Jr. and M. F. Hawthorne, *Inorg. Chem.*, 13 (1974) 2312.

321 L. I. Zakharkin and N. F. Shemyakin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1974) 940.

322 L. I. Zakharkin and N. F. Shemyakin, *Zh. Obshch. Khim.*, 44 (1974) 1085.

323 T. Yamamoto and L. J. Todd, *J. Organometal. Chem.*, 67 (1974) 75.

324 J. L. Little, S. S. Pao, and K. K. Sugathan, *Inorg. Chem.*, 13 (1974) 1752.

325 M. Benmalek, H. Chermette, C. Martelet, D. Sandino, and J. Tousset, *J. Inorg. Nucl. Chem.*, 36 (1974) 1359.

326 I. W. Flynn and I. B. R. Bowman, *Comp. Biochem. Physiol. B*, 48 (1974) 261.