# ARSENIC

## ANNUAL SURVEY COVERING THE YEAR 1971

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## 1. BOOKS AND REVIEWS

Although no books or review articles devoted to arsenic or other Group V representative elements have been published in 1971, several books and articles included data on chemical or physical properties of organoarsenicals. In a review article on the redistribution reaction, Moedritzer [1] summarized redistribution reactions of organic arsenic compounds. In a report on the spectroscopic properties of inorganic and organometallic compounds, such physical properties as NMR, IR, and NQR spectra of organic compounds containing one or more arsenic atoms were mentioned [2]. In a monograph on the thermochemistry of organic and organometallic compounds, the rather scanty thermochemical data on organoarsenic compounds were summarized [3]. A few organic compounds containing As-Ge bonds as well as As-C bonds have been mentioned in a monograph on organogermanium compounds [4].

In a review article from 1970 which appeared too late to be included in the 1970 review of arsenic compounds, Davis and Gray [5] listed alkali metal and magnesium derivatives of organoarsenic compounds together with similar alkali metal and magnesium compounds of a number of other metals. A review article on steric effects in substituted halocarbonyl derivatives of molybdenum and tungsten included organophosphorus, arsenic, and antimony compounds as ligands [6].

## 2. PRIMARY AND SECONDARY ARSINES

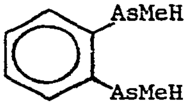
Cullen and Leeder [7] have studied the rate of the exchange reaction:

$$Me_2AsD + Et_2AsH \rightleftharpoons Me_2AsH + Et_2AsD$$

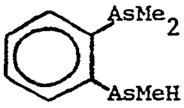
The reaction rate was easily determined by conventional PMR techniques. The reaction was studied both for the neat liquids and in solution in diethyl ether-$d_{10}$; at 35° rate constants of $5.9 \times 10^{-5}$ and $4.95 \pm 0.25 \times 10^{-5}$ liter mole$^{-1}$ s$^{-1}$, respectively, were obtained. The equilibrium constants under these conditions were $1.335 \pm 0.020$ and $1.2 \pm 0.1$, respectively. The rate of the reaction between $Me_2AsH$ and $(CF_3)_2AsD$ was found to be too fast to measure.

By the use of $^{14}$C-labelled methylcob(III)alamin and of $^{74}$As-labelled disodium arsenate McBride and Wolfe [8] were able to demonstrate that both whole cells and cell extracts of *Methanobacterium* strain M.O.H. were able to reduce and methylate the arsenic to dimethylarsine. The methyl donor of choice was shown to be methylcobalamin. The pathway involved the reduction of arsenate to arsenite followed by methylation to form methanearsonic acid. The methanearsonic acid was then reductively methylated to form dimethylarsine.

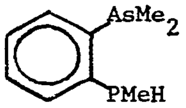
Carlton and Cook [9] have reported the synthesis and PMR spectra of the three interesting arsines I, II, and III.



I



II



III

The secondary arsine I was prepared by treatment of the corresponding primary arsine with *n*-butyllithium followed by the addition of methyl iodide. The arsine II was obtained by cleavage of a methyl group from *o*-phenylenebis(dimethylarsine) by sodium in liquid ammonia. Approximately 15-25% of phenyldimethylarsine was obtained by the same reaction. The final product III was obtained from *o*-dimethylarsinophenylphosphine.

The PMR spectra of the compounds were of particular interest. Compound II showed the presence of three magnetically nonequivalent methyl groups. The spectrum of I showed two overlapping quartets due to nonequivalent protons attached to arsenic in *dl* and *meso* forms.

King and Kapoor [10] have introduced a novel method of preparing polytertiary phosphines and arsines by the addition of compounds containing the P-H or As-H bond to unsaturated linkages in the presence of a base catalyst. Although this paper is mainly devoted to phosphorus compounds, the three organoarsenicals $Ph_2PCH_2CH_2AsPh_2$, $PhP(CH_2CH_2AsPh_2)_2$, and *trans*-$Ph_2PCH{=}CHAsPh_2$ were also prepared. The last compound was obtained from diphenylethynylphosphine and diphenylarsine. Both $^1H$ and $^{31}P$ NMR spectra were given and all the compounds were characterized by elementary analyses.

The base-catalyzed addition of both diphenylphosphine and diphenylarsine to vinyl isocyanide in boiling benzene has also been reported by King and Efraty [11]. The arsenic product $Ph_2AsCH_2CH_2NC$ was a liquid obtained in 31% yield. Both the phosphorus and arsenic compounds formed complexes with the norbornadiene chromium complex $C_7H_8Cr(CO)_4$ of the approximate composition $(Ph_2MCH_2CH_2NC)_4Cr_3(CO)_{12}$ where M = P or As. The compound $Ph_2AsCH_2CH_2NC$ was characterized by elemental analysis, molecular weight data, and by IR and PMR spectra.

A series of compounds containing As-Sn bonds has been reported by Anderson and Drake [12]. The organoarsenic compounds described were $Me_3SnAsHPh$, $Me_3SnAsMe_2$, $Me_3SnAsPh_2$, $(Me_3Sn)_2AsMe$, and $(Me_3Sn)_2AsPh$. The synthetic methods used for the preparation of these compounds as well as compounds containing an As-Sn but no As-C bond were listed in detail. The compounds were characterized by IR, NMR, and molecular weight determinations.

## 3. TERTIARY ARSINES

### A. Preparation

The preparation of three new ligands $(o\text{-}CH_2{=}CHC_6H_4)_3M$, where M = P, As, or

Sb, has been reported by Hall and Nyholm [13]. They were obtained from the Grignard reagent prepared from *o*-bromostyrene and the appropriate $MCl_3$. Several complexes were prepared by using these three compounds as bidentate ligands to platinum.

Although the customary method of preparing tertiary arsines employs Grignard reagents and arsenic trichloride, other trivalent arsenic compounds can be used. Kamai and co-workers [14] have prepared tertiary arsines from Grignard reagents and triisopentyl arsenite. The yields were moderate (43.5–81.5%). Tris(*p*-ethoxyphenyl arsine could not be obtained by this reaction while from *o*-tolylmagnesium bromide, di-*o*-tolylarsinous acid was obtained. The densities and refractive indices (but no spectral data) for most of the arsines prepared were listed.

The reactions of the dimethylarsenide ion with organic halides have been found to be more complex than the analogous reactions of the diphenylarsenide ion. Feltham and Metzger [15] have reported that $NaAsMe_2$ reacted with *o*-dichlorobenzene to give a mixture of dimethylarsine (identified as dimethylarsenic acid), *o*-bis(dimethylarsino)benzene, dimethylphenylarsine, 5,10-dimethyl-5,10-dihydroarsanthrene, trimethylarsine, and methylbis(*o*-dimethylarsinophenyl)-arsine. The last two compounds were not isolated from the reaction mixture but were believed to be present because of certain peaks found in the mass spectrum of the crude oil obtained after hydrolysis of the reaction mixture. The reaction of $NaAsMe_2$ with *cis*-1,2-dichloroethylene gave a mixture of *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene, with the *trans* isomer predominating. 1,2-Dibromoethylene and $NaAsMe_2$ gave a mixture of bis(dimethylarsino)ethyne and 1-bromo-1,2-*cis*-(dimethylarsino)ethylene. An improved synthesis of *cis*-1,2-bis(dimethylarsino)ethylene by the hydroboration of bis(dimethylarsino)ethyne was described. 8-(Diphenylarsino)quinoline (as well as the corresponding phosphorus compound) was prepared from $NaAsPh_2$ (or $NaPPh_2$) and 8-chloroquinoline. The mass spectra of most of the arsenic compounds prepared were reported and fragmentation patterns were suggested.

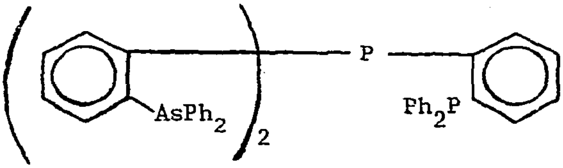
Kuo and Jolly [16] have studied the reaction of the $AsH_2^-$ ion with aryl halides. The overall reaction was:

$$3AsH_2^- + 3PhX \longrightarrow 2AsH_3 + Ph_3As + 3X^-$$

When iodobenzene was the aryl halide no triphenylarsine was found and the only organic arsenical isolated was tetraphenyldiarsine. The other products were arsine, hydrogen, and benzene. With bromobenzene, in addition to arsine and triphenylarsine, tetraphenyldiarsine, benzene, arsine, and diphenylarsine were isolated. With chlorobenzene triphenylarsine but no tetraphenyldiarsine was found. When $KAsD_2$ was allowed to react with bromobenzene essentially pure $C_6H_5D$ was obtained. The authors presented plausible mechanisms to account for their results.

In a study of coordination compounds of mercury(II) Sandhu and Singh [17] have reported on the synthesis of three new tertiary arsines: 2-carbomethoxphenyldiphenylarsine, 2-carboxmethoxyphenyldimethylarsine, and 2-carbomethoxyphenyldi-*p*-tolylarsine. They were all prepared by esterification of the corresponding carboxyarsines with diazomethane.

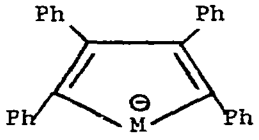
Although quadridentate ligands such as $(o\text{-}Ph_2AsC_6H_4)_3As$ or $(o\text{-}Ph_2AsC_6H_4)_3P$ can be readily prepared, Dawson and Venanzi [18] were interested in obtaining ligands in which different ligand groups were attached to the central atom of the ligand. They have outlined a general scheme for preparing a variety of such compounds and then applied this general scheme to the preparation of the compound IV.



IV

The spin-decoupled $^{32}$P-{$^{1}$H} NMR spectrum of this compound was reported, and chemical shifts of the two phosphorus atoms were assigned.

The cleavage of phenyl groups from triphenylphosphine, -arsine and -stibine by an alkali metal is a well-known reaction. Braye and co-workers [19] have studied the cleavage of phenyl groups by the action of an alkali metal on pentaphenylphosphole and pentaphenylarsole. With the phosphole, the phenyl group attached to the phosphorus was cleaved by Li, Na, or K to give the ion V (M = P).



V

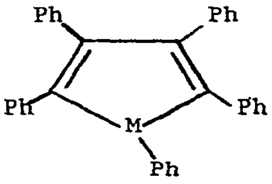
In contrast pentaphenylarsole reacted with both lithium and potassium with loss of arsenic and the formation of 1,2,3-triphenylnaphthalene. With sodium, however, pentaphenylarsole behaved in a similar manner to the phosphole and gave the ion V, M = As. The cleavage reaction was carried out in boiling toluene and was followed by the addition of methyl iodide; the product isolated was 1-methyl-2,3,4,5-tetraphenylarsole. Oxidation of this arsine with hydrogen peroxide gave the arsine oxide.

In a series of interesting reactions, Ang and Ho [20] have shown that bis(trifluoromethyl)nitroxide, $(CF_3)_2NO$, reacted with tris(trifluoromethylarsine to form three different products, $(CF_3)_2NOAs(CF_3)_2$, $[(CF_3)_2NO]_2AsCF_3$, and $[(CF_3)_2NO]_3As$. The first two products were formed when the reactants were allowed to react at room temperature; the products formed depended only on the ratios between the reactants. The third product, $[(CF_3)_2NO]_3As$, was formed at a 6:1 ratio of $(CF_3)_2NO$ to $(CF_3)_3As$ at a temperature of 70°. The IR spectra of the products were given and assignments of the various bands were made.

1,1'-Disubstituted ferrocenes have been difficult to prepare. Bishop and co-workers [21] have now demonstrated that ferrocene can be dilithiated in high yield by the use of *n*-butyllithium and N,N,N',N'-tetramethylethylenediamine. The dilithiated product, which was pyrophoric, reacted readily with halophosphines or haloarsines to yield the ferrocene diphosphines or diarsines. Thus were prepared ferrocene-1,1'-bis(dimethylarsine), its mono- and dimethiodide and arsine sulfide, as well as ferrocene-1,1'-bis(diphenylarsine), its dimethiodide, and arsine sulfide. Both PMR and infrared data were included.

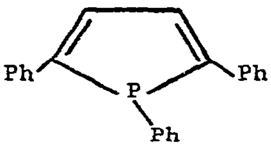
### B. Spectra

The absorption and the fluorescence spectra of the three heterocyclic pentadienes VI, as well as the two related compounds VII and VIII, have been compared [22]. There was little difference in their absorption spectra, but

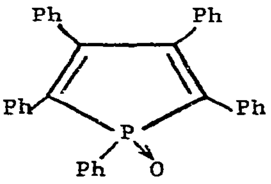


VI

(a, M = N; b, M = P;
c, M = As)



VII



VIII

there was considerable difference in the radiative lifetimes of several of the compounds. The values of the quantum yield of fluorescence ($\phi$) decreased in going from VIa to VIc because of an increase in quenching efficiency with increasing atomic number of the hetero atom.

The mass spectra of five derivatives of 5,10-dihydrophenarsazine have been reported by Tou and Wang [23]. The results were quite similar to those reported earlier by Earley and Gallagher [24]. Tou and Wang also studied the pyrolysis of the phenarsazine derivatives and concluded that the pyrolytic decompositions closely parallel the ion fragmentations.

The photolysis of di-*t*-butyl peroxide in the cavity of an ESR tube in the presence of a variety of alkyl organometallic compounds resulted in an $S_H2$ reaction at the metal center and the spectrum of the displaced alkyl radical could be observed [25]. Among the compounds studied in this manner was tri-*n*-butylarsine and the radical observed was the *n*-butyl radical.

A study of the Mössbauer parameters of a series of adducts of tin(IV) halides with nitriles or with tertiary arsines, phosphines, or arsines has been reported by Cunningham, Frazer, and Donaldson [26]. The attempted preparation of adducts between tin(IV) halides and tertiary stibines is reported in the Antimony section. The arsenic compounds prepared were $SnCl_4 \cdot 2AsPh_3$, $SnBr_4 \cdot 2AsPh_3$, $SnCl_4 \cdot 2AsEt_3$, and $SnBr_4 \cdot 2AsEt_3$. The chemical shifts and quadrupole splitting (when observed) for the various compounds were reported. The IR and Raman spectra for the phosphine and arsine adducts were also reported. Although an increase in quadrupole splitting of tin halide 1:2 complexes had been previously attributed to a decrease in strength of the donor-acceptor bonds, no such relationship was found with the arsine and phosphine adducts reported in this paper.

Zykova and co-workers [27] have examined the PMR spectra of the methyl and methylene protons of a series of arsenic compounds of the type EtAsRR', where R and R' were phenyl, alkoxy, and halogen groups, as well as ethyl groups. In those cases where R and R' were both electron-attracting groups there was a considerable shift of the $\delta$ value of the methylene protons to higher fields. The shift was less marked or zero when two ethyl groups were present in the molecule. The protons of the methyl group were essentially unaffected and the authors used the increment $\Delta = \delta(CH_2) - \delta(CH_3)$ as a measure of the effect of electron-attracting substituents on the chemical shifts of the methylene protons. The chemical shift of the methylene protons of triethylarsine oxide was also examined and found to have an intermediate value between those of triethylarsine and tetraethylarsonium salts. From this result the authors concluded that the "positive charge" on the arsenic was in the order $Et_3As < Et_3AsO < Et_4As^+$.

In a previous paper [28] Yoder, Tuck, and Hess have reported on the $^{13}C$-H coupling constants of compounds of the type $XC_6H_4Me$ or $XC_6H_4YMe_n$ where Y = C, N, or O, and $n$ = 3, 2, or 1, respectively. A plot of the coupling constants *vs.* the Hammet $\sigma$ constants for the group X, gave straight lines whose slopes were indicative of the ability of the group Y to transmit electrical effects to X. The work has now been extended to compounds of the type $XC_6H_4YMe_n$ where Y = Si and Ge and $n$ = 3, Y = P or As, $n$ = 2, and Y = S, $n$ = 1 [29]. A number of new tertiary arsines were prepared by standard methods and their chemical properties reported. Unfortunately, because of inability to find common solvents and because of poor correlation coefficients the authors were unable to draw any satisfactory conclusions as to the ability of the Group V elements to transmit their electrical effects to the substituent group.

In a paper largely devoted to the UV spectra of organophosphorus compounds, Shagidullin and Chernova [30] report on the UV spectra of two tertiary arsines, $p$-$MeC_6H_4As(n\text{-}Pr)_2$ and $p$-$MeOC_6H_4AsEt_2$. In the spectrum of the tolyl compound three bands were seen and were assigned as K, R, and B bands. The band $\lambda_{max}$ = ∿245 nm, log $\varepsilon$ = 3.96 was believed to be associated with the $n \rightarrow \pi^*$ transition. In the anisyl compound the K band was expected to exhibit a bathochromic shift, the R band a hypsochromic shift. The spectrum of the compound revealed that the K and R bands were combined. The R band was found to disappear when the anisyl arsine was oxidized to the arsine oxide.

The IR spectra both in $CCl_4$ solution and in perfluorocarbon or Nujol mulls and the Raman spectra in the solid state and in $CHCl_3$ solution were reported for $(p\text{-}FC_6H_4)_3As$, $(p\text{-}ClC_6H_4)_3As$, $(m\text{-}FC_6H_4)_3As$, $(m\text{-}ClC_6H_4)_3As$, and also for the four corresponding arsine oxides [31]. By considering the *para* compounds as possessing $C_{2v}$ symmetry and the *meta* compounds $C_s$ symmetry, assignments for all of the bands were made.

The preparation of $(m\text{-}FC_6H_4)_3As$, $(p\text{-}FC_6H_4)_3As$, $(m\text{-}ClC_6H_4)_3As$, and $(p\text{-}ClC_6H_4)_3As$ by a Grignard reaction has been described by de Ketelaere and co-workers [32].

The arsines were oxidized to the corresponding arsine oxides by hydrogen peroxide in acetone solution. The PMR spectra of all of the compounds were given and for $(p\text{-}FC_6H_4)_3As$ and the corresponding oxide coupling constants were calculated. Similar constants were also calculated for $(p\text{-}ClC_6H_4)_3As$ and the corresponding oxide. The $^{19}F$ NMR for the fluoro compounds were also given.

The mass spectra of triethyl-, tri-*n*-propyl- and tri-*n*-butylarsines and of tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butyldiarsines have been reported by Bogolyubov and co-workers [33]. The mass spectra of the trialkylarsines were similar to other alkyl derivatives of Groups V and VI. There is a fairly intense molecular ion followed by loss of a $C_nH_{2n}$ fragment. After a second As-C bond was broken, a loss of arsenic led to the formation of a group of hydrocarbon ions. The mass spectra of the tetraalkyldiarsines were somewhat different from that of the trialkylarsines. The energy of dissociation of the M-M bond in a series of Group V compounds ($R_2M\text{-}MR_2$) and Group VI compounds (RM-MR), where R is ethyl except for $Me_2N\text{-}NMe_2$, was compared with the energy of dissociation of the diatomic molecules of the Group V and VI elements. It was concluded that alkylation lowered the bond energy, particularly in the case of oxygen and nitrogen.

In a paper devoted mainly to the preparation of phosphino acetylenes, Carty and co-workers [34] have described two arsenic-containing acetylenes, $Ph_2AsC{\equiv}CCF_3$ and $Ph_2PC{\equiv}CAsPh_3$. The IR and mass spectra of the compounds were listed, and suggested pathways for the fragmentations were given.

Both the ultraviolet spectra and the ionization potentials as determined by photoelectron spectroscopy of a series of unsaturated fluorocarbon derivatives of N, P, As, and Sb have been reported by Cullen and co-workers [35]. Many of the olefin compounds showed absorption in the low energy region which was assigned either to an $n \rightarrow \pi^*$ transition or to charge transfer. The compound $As(CF{=}CF_2)_3$ does not absorb in this region presumably due to delocalization of the arsenic lone pair. The *cis*- and *trans*-isomers of $Me_2AsC(CF_3){=}C(CF_3)H$ showed significantly different UV spectra. The *cis*-isomer absorbed approximately twice as intensely as the *trans*-isomer and the absorption was more solvent dependent. This result has been attributed to steric interactions in the excited state. The acetylene derivatives showed a low energy transition which has also been attributed to a $n \rightarrow \pi^*$ transition. A high energy band in these compounds was attributed to a $\pi \rightarrow \pi^*$ transition. The effect of structure on the ionization potentials of several of these organoarsenic compounds was also discussed.

In a paper devoted to the calculation of valence force constants and mean amplitudes of vibration from available data for the compound $As(C{\equiv}CH)_3$, Smit and Dijkstra [36] considered both a linear and a bent configuration for the As-C≡C-H grouping and concluded that either model reproduced the observed frequencies equally well. The fact that the As-C stretching force constant for $As(C{\equiv}CH)_3$ was somewhat higher than that reported for trimethylarsine may indicate some $p_\pi - d_\pi$ bonding in the acetylenic compound, but this would be somewhat less than in the corresponding triethynylphosphine.

In continuation of earlier work on the electron-donor capacity of Group V elements, Épshtein and co-workers [37] have investigated the infrared spectra of phenol when complexed with triphenylmethane and with compounds of the type $Ph_3M$, where M = N, P, As, or Sb. The infrared spectra suggested two types of bonding, namely a π-complex between the phenolic hydrogen and the π system of the $Ph_3M$ molecule and a "*p*-complex" between the phenolic proton and the heteroatom. The energies of formation of both types of bonding were calculated; the energies of the H-complexes of the various hetero-atoms were in the order $P > Sb \sim As > N$.

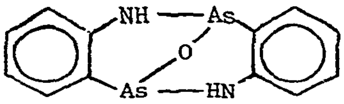
## C. Use as Ligands

The cleavage of bis(dithiolene)-iron dimers by a number of Lewis bases to form five-coordinate adducts has been reported by Balch [38]. Among the bases studied were both triphenylarsine and triphenylarsine oxide.

Cheney and Shaw [39] have isolated *dl* and *meso* forms of the complexes $MX_2L_2$, where M = Pt or Pd, X = Cl, Br, or I, and L = $(PhMeAsCH_2)_2$. Both modifications (where X = Cl) reacted with methyllithium to give the corresponding dimethyl compounds $MMe_2L_2$. The latter compounds underwent oxidative addition reactions with methyl halides, acetyl halides, and allyl chloride to give compounds of the type $MMe_2L_2(R)X$ (where R = Me, MeCO, or $CH_2{=}CH{-}CH_2$).

The two interesting compounds ferrocene-1,1'-bis(dimethylarsine) and ferrocen 1,1'-bis(diphenylarsine) have been prepared and studied as ligands to the transiti metals Pt, Pd, and Ni [40]. The bis(dimethyl) compound, when in excess, formed complexes in which the Pt or Pd was five or four coordinate, whereas the more sterically crowded bis(diphenylarsine) formed only the simpler complexes $LPtX_2$ and $LPdX_2$. The only nickel complexes prepared also contained a CO ligand.

Three new tertiary arsines for use as ligands in coordination chemistry have been reported by Chiswell and Verral [41]. 1-Amino-2-(diphenylarsino)ethane was prepared from 1-chloro-2-(diphenylarsino)ethane by means of the Gabriel synthesis. The two compounds *o*-dimethylarsinoaniline and *o*-diphenylarsinoaniline were both obtained by the same method, namely the reaction of the Grignard reagents MeMgI or PhMgBr with the anhydride $[C_6H_4As(NH)]_2O$. The latter compound was obtained by hydrolysis of *o*-dichloroarsinoaniline hydrochloride with aqueous ammonia, and refluxing of the product with ethanol. The anhydride was formulated as:



Although trialkyl- and triarylstibines have frequently been used as ligands in coordination chemistry, relatively few stibines have been synthesized for use primarily as ligands. Cook, McAuliffe, and Meek [42] have reported on the synthesis of dimethyl(*o*-dimethylarsinophenyl)stibine. The details of the synthesis as well as mention of several coordination compounds of this ligand with nickel compounds are more fully described in the Antimony section.

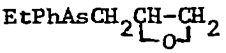
Both arsenic and phosphorus compounds have been prepared which serve as quadridentate ligands to metal atoms. Often the structural and physical properties of the complexes are not readily accountable for by a consideration of only the electronic properties of the donor ligands. With such a view in mind Dawson and co-workers [43] have analyzed the effect of geometric factors imposed by the ligand structure on the properties or on the preparation of a group of quadridentate ligands of the type $L'(o\text{-}C_6H_4LR_2)_3$, where L and L' were such atoms as N, P, As, and Sb, or of the type $L'(o\text{-}C_6H_4LR)_3$, where L' is P and L is S or Se. The authors arrived at a set of match or mismatch parameters of these tripod ligands compared with some monodentate ligands.

A number of interesting compounds derived from $Mn_2(CO)_{10}$ and a group of arsenical ligands of the type $Me_2AsX$ have been reported by Grobe and Kober [44]. Thus, the compound $Mn_2(CO)_8AsMe_2I$ was readily prepared from $Me_2AsI$ and $Mn_2(CO)_{10}$, but the corresponding compounds from $Me_2AsBr$ and $Me_2AsCl$ could not be prepared directly. Two other ligands which did react with $Mn_2(CO)_{10}$ to give compounds of the type $Mn_2(CO)_8AsR_2Y$ were $Me_2AsP(CF_3)_2$ and $(CF_3)_2AsPMe_2$. The iodine in $Mn_2(CO)_8AsMe_2I$ was readily replaced by reaction with various compounds to give other derivatives of the type $Mn_2(CO)_8AsMe_2X$, where X was $SCF_3$, SMe, Cl, H, or $PMe_2$.

A large number of other papers describing the use of tertiary arsines as ligands have also been published. The metals coordinated to the arsenic in the complexes included chromium [45-52], cobalt [49, 53-61], copper [62-69], gold [70-73], iridium [74-83], iron [49, 57, 84-88], manganese [45, 57, 89-91], mercury [92], molybdenum [45-47, 49-52, 94-100], nickel [49, 101-107], osmium [108, 109], palladium [110-122], platinum [110, 113-115, 118, 119, 123-139], rhenium [89, 94], rhodium [78-80, 82, 116, 140-147], ruthenium [85, 148-155], silver [73, 156], tin [157], titanium [157], tungsten [45-47, 49-52, 96], and vanadium [158].

## D. Other Chemical and Physical Properties

Gatilov and co-workers, who have contributed many articles on the optical activity of tertiary arsines, have reported [159] on the optical activity of the three (ethylphenylarsino)benzoic acids, *o*-, *m*- and *p*-$HOOCC_6H_4AsEtPh$, together with the methyl esters of these compounds. With the acids the $[\alpha]_D^{20}$ was in the order *o*, +18.36; *m*, +16.63; and *p*, +12.75. The corresponding (-) enantiomers gave similar absolute values. A similar decrease in activity in going from *ortho* to *para* was noted for the methyl esters. The authors attributed this decrease in optical activity to an increase in the distance of the substituent from the center of assymetry

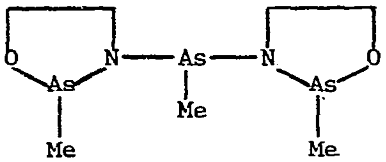
Gatilov and co-workers [160] have also prepared (ethylphenylarsino)acetic acid by oxidation of allylethylphenylarsine with either potassium permanganate or hydrogen peroxide followed by reduction of the arsine oxide by sulfur dioxide. In addition to the arsinoacetic acid, the corresponding 1,2-propanediol $EtPhAsCH_2CHOHCHOH$ and the epoxy compound  $EtPhAsCH_2\underbrace{CH-CH_2}_{O}$ were obtained in small yield. (Ethylphenylarsino)acetic acid was resolved by means of the diastereomeric salts formed with (-)-α-methylbenzylamine. Only the (+)-$EtPhAsCH_2COOH$, $[\alpha]_D^{20}$ = +2.65, was obtained. Oxidation of this optically active acid with hydrogen peroxide gave the racemic arsine oxide, but reaction of the active acid with sulfur gave an optically active sulfide, $[\alpha]_D^{20} = +3.98$.

In a paper devoted to the optical activity of organic compounds of the Group V elements, Kessler [161] discussed the optical activity of tertiary arsines and of arsonium salts.

Based on Pauling's assumption that zero or very small electronegativity differences between atoms should give little or no dipole moments in compounds, Faget and Mauret [162] have calculated an apparent moment due to the contribution of the lone pair of electrons in the hydrides $PH_3$, $AsH_3$, $SbH_3$ and the alkyl derivatives $R_3P$ and $R_3As$. A plot of the percent *p*-character for the bonds involved *vs*. the lone-pair dipole moment gave a straight line which passed through the origin.

## 4. AMINOARSINES

The reaction of arsenic trichloride and of methyldichloroarsine with aminoalcohols has been utilized by Sommer and co-workers [163] for the preparation of interesting arsenic heterocyclic compounds. Most of the compounds do not contain a C-As bond, but the reaction of methyldichloroarsine and ethanolamine led to the formation of bis(2-methyl-1,2,3-oxarsazolidino)methylarsine (IX).

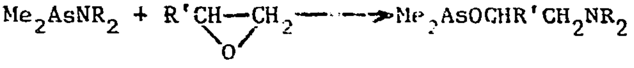


IX

The compound was characterized by elementary analysis and molecular weight.

The reaction of dialkylaminodimethylarsines, $R_2NAsMe_2$, where R = Me or Et, with β-propiolactone resulted in alkyl-oxygen cleavage and formation of the adduct $Me_2AsO_2CCH_2CH_2NR_2$ [164]. The adducts were sensitive to protic solvents and were cleaved by methanol to give methyl dimethylarsinite which was identified as dimethylchloroarsine after treatment with hydrogen chloride. Treatment of β-propiolactone with dimethyl(pyrrolidino)arsine gave poly-β-propiolactone in 90% yield.

The study was also extended to the reaction of dialkylaminodimethylarsines and monosubstituted ethylene oxides. The reaction proceeded in the following manner:



$$Me_2AsNR_2 + R'CH{-}CH_2 \ (\text{-O-}) \longrightarrow Me_2AsOCHR'CH_2NR_2$$

PMR data on the adducts and the degredation products produced when the adducts were treated with methanol followed by hydrogen chloride in ether were used to establish the structure of the adducts. The conformation of the adducts produced from 1,1,1-trichloro-2,3-epoxypropane and several dialkylaminodimethylarsines was deduced from the PMR data.

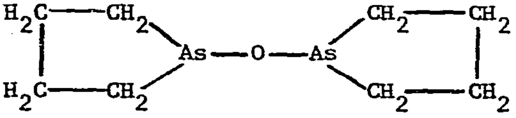
## 5. HALOARSINES

Tertiary polyfluoroalkylarsines were readily prepared by the reaction of $AsF_3$ with fluoroolefins in the presence of $SbF_5$ [165]. Thus, $AsF_3$ and $CF_2{=}CH_2$ gave a 42% yield of $(CF_3CH_2)_3As$. Other arsines prepared by this method were $(CF_3CHF)_3As$ and $(C_2F_5)_3As$. The latter compound was obtained from $CF_2{=}CF_2$ and $AsF_3$ which also gave a 30% yield of $(CF_2CH_2)_2AsF$

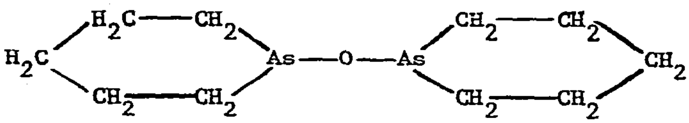
Very similar work to the above has been described in a British patent [166]. The catalyst in this case was $SbF_3$. Thus, $CF_2{=}CF_2$ and $AsF_3$ gave $(CF_3CF_2)_3As$ and $(CF_3CF_2)_2AsF$. Similarly, $CF_2{=}CFCl$ and $AsF_3$ gave $(CF_3CFCl)_2AsF$.

The infrared spectra (from 4000 to 33 $cm^{-1}$) and the Raman spectra of the compounds $MeAsCl_2$, $MeAsBr_2$, $MeAsI_2$, and $CD_3AsI_2$ have been reported by Durig and co-workers [167] On the basis of $C_s$ symmetry for these molecules, all of the fundamental vibrational frequencies were assigned. The barrier to internal rotation for the molecule $MeAsBr_2$ was calculated to be 461 ± 30 $cm^{-1}$ or 1.32 ± 0.08 kcal/mole.

In continuation of previous work on heterocyclic arsenic compounds, Sommer [168] has prepared the two oxides X and XI by hydrolysis of the corresponding chloroarsines.

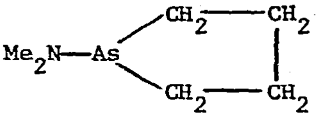


X



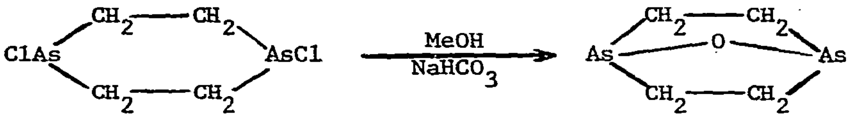
XI

The reaction of 1,4-tetramethylenebis(magnesium bromide) with dichlorodimethylaminoarsine gave XII which was readily hydrolyzed to X.



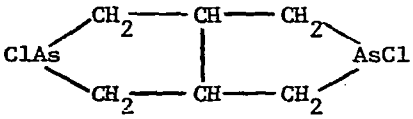
XII

The oxides X and XI were also obtained, but only in low yields, by the action of the Grignard reagents obtained from 1,4-dibromobutane or 1,5-dibromopentane and finely powdered arsenic(III) oxide. The two oxides X and XI were readily oxidized with hydrogen peroxide to the corresponding arsenic acids. 1,4-Diphenyldiarsenane reacted with $AsCl_3$ in a sealed tube to give 1,4-dichlorodiarsenane, XIII. This with sodium bicarbonate in methanol gave a small amount of the oxide XIV together with larger amounts of a dimeric oxide:

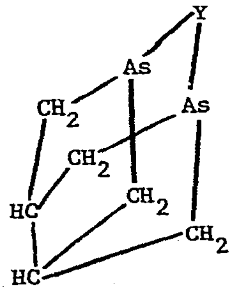


XIII XIV

The previously prepared 2,6-dichloro-2,6-diarsabicyclo[3,3,0]octane (XV) reacted with $H_2O$, $H_2S$, or $MeNH_2$ to give the tricyclo compounds XVI.



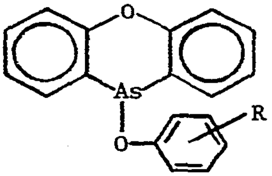
XV



XVI Y = O, S, or NHMe

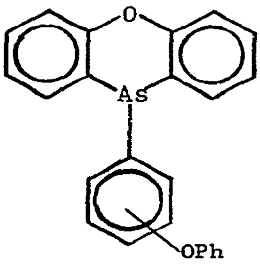
## 6. OTHER TRIVALENT ARSENIC COMPOUNDS

Phenoxarsines of the type XVII, which are useful as pesticides and as stabilizers for polyvinyl chloride, have been obtained by the reaction of 10,10'-oxybisphenoxarsine with phenol or with substituted phenols [169].



XVII

A second patent describes the preparation of phenoxyphenylphenoxarsines XVIII from the reaction of 10-chlorophenoxarsine with the appropriate phenoxyphenylmagnesium chloride [170]. The compounds were useful as fungicides, herbicides, and insecticides.



XVIII

In a study devoted to the bactericidal and other antimicrobial properties of compounds which react with thiol groups, the two compounds $p$-$RC_6H_4As(SCH_2CO_2H)_2$, where R = Cl or $NH_2$, were shown to have a broad spectrum of antibacterial activity [171].

In a continuation of previous studies dealing with the reaction of alkyl halides with esters of dialkyl- or alkylarylarsinous acids, Abalonin, Chernokal'ski and co-workers [172] have examined the IR and proton NMR spectra of the products and concluded that, contrary to previous statements, the products were tetraalkyl- or trialkylphenylarsonium salts.

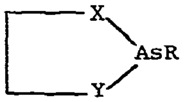
In a study of azides of the type $Me_2MN_3$, where M = As, Bi, or Tl, Müller [173] prepared azidodimethylarsine by the reaction between dimethyliodoarsine and silver azide. The compound was a colorless liquid, b.p. 136°, and was monomeric in benzene. The IR and Raman spectra of the compound were reported and confirmed the monomeric structure.

When trigermylarsine $(GeH_3)_3As$ was allowed to react with dimethylchloroarsine in a vacuum line at -78°, chlorogermane was evolved [174]. The postulated reaction was:

$$(GeH_3)_3As + Me_2AsCl \longrightarrow Me_2AsAs(GeH_3)_2 + GeH_3Cl$$

The $Me_2AsAs(GeH_3)_2$ was not isolated or otherwise characterized. On warming to room temperature, $Me_2AsGeH_3$ and a yellow solid were obtained. The yellow solid was believed to be $(GeH_3As)_n$ where $n = 5$.

In a preliminary communication Anderson and Cragg [175] reported on the mass spectra of a series of heterocyclic arsenic compounds of the type XIX (where X = O or S and Y = O or S; or X = O and Y = NMe; and R = Ph, Et, $Me_2N$, or $Et_2N$).



XIX

In all compounds the R was readily lost to give an "arsenium" ion. This ion must be quite stable and generally exceeds the parent ion in intensity. When R was phenyl, a rearrangement occurred resulting in the formation of the tropylium ion.

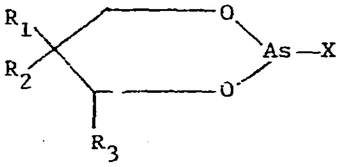
In describing a series of thiodimethylboranes of the type $R_nSBMe_2$ and the reactions of these compounds, Vahrenkamp [176] prepared the arsenic-containing borane $Me_2AsSBMe_2$. It was obtained by the reaction between $(Me_2As)_2S$ and $Me_2BI$:

$$(Me_2As)_2S + Me_2BI \longrightarrow Me_2AsSBMe_2 + Me_2AsI$$

It was also prepared from the tin compound, but the two products could not be separated by distillation:

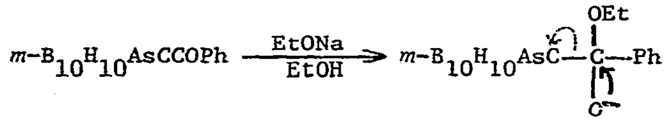
$$Me_2AsCl + Me_3SnSBMe_2 \longrightarrow Me_2AsSBMe_2 + Me_3SnCl$$

A study of the dipole moments of a number of 2-substituted 1,3-dioxaarsole compounds of the type



(where X was Cl, Ph, or $p$-$NO_2C_6H_4$ and the R groups were either H or Me) led to the conclusion that the most favorable ring conformation was a chair form with the X group equatorial [177].

The chemical reactions of *m*-carbaarsaborane (*m*-$B_{10}H_{10}AsCH$) were reported by Zakharkin and Kyskin [178]. The compound was readily metalated by phenyllithium and the product converted to the acid *m*-$B_{10}H_{10}AsCCOOH$. This acid gave an acid chloride with $PCl_5$ which underwent a Friedel-Crafts reaction to give the ketone *m*-$B_{10}H_{10}AsCCOPh$. Two other ketones prepared from the acid chloride were *m*-$B_{10}H_{10}AsCCOCB_{10}H_{10}CMe$-*m* and *m*-$B_{10}H_{10}AsCCOCB_{10}H_{10}P$-*m*. The ketone *m*-$B_{10}H_{10}AsCCOPh$ was readily cleaved by catalytic amounts of sodium ethylate in ethanol or wi NaOH in ethanol:



$$m\text{-}B_{10}H_{10}AsCCOPh \xrightarrow[EtOH]{EtONa} m\text{-}B_{10}H_{10}AsC{-}\overset{OEt}{\underset{O^-}{C}}{-}Ph$$

$$\longrightarrow m\text{-}B_{10}H_{10}AsC^- + PhCO_2Et$$

$$m\text{-}B_{10}H_{10}AsC^- + EtOH \longrightarrow m\text{-}B_{10}H_{10}AsCH$$

Cleavage of the ketone $m$-$B_{10}H_{10}AsCCOCB_{10}H_{10}CMe$-$m$ with NaOH and ethanol yielded $m$-$B_{10}H_{10}AsCH$ and $m$-$MeCB_{10}H_{10}CCO_2Na$. From this latter result it was concluded that the $m$-carbaarsaborane system was a stronger electron acceptor than the $m$-carborane system. A similar cleavage of $m$-$B_{10}H_{10}AsCCOCPB_{10}H_{10}$-$m$ indicated that the $m$-carbaphosphaborane system was a stronger electron acceptor than the $m$-carbaarsaborane system. The $pK_a$ of the $m$-carbaarsaboranecarboxylic acid was found to be 3.27 ± 0.05 in 50% alcohol.

The report of an unsuccessful attempt to prepare mixed esters of the type RAs(OR')SR" by several types of reaction has been given by Chadaeva and co-workers [179]. For example, the reaction of PhAs(Cl)OEt with EtSNa gave a mixture of $PhAs(OEt)_2$ and $Ph(SEt)_2$. However, mixed esters from 2-chloro-1,3,2-oxathiaarsolane were obtained:

The interesting compound $PhAsCl_3N_3$ was prepared by the reaction of chlorine azide with phenyldichloroarsine in carbon tetrachloride solution [180]. The chloroazide was unstable at room temperature and slowly evolved chlorine and nitrogen. The decomposition was accelerated at higher temperatures but the reaction was not explosive:

$$PhAsCl_3N_3 \longrightarrow PhAsClN + Cl_2 + N_2$$

The product PhAsClN was best prepared at 100° *in vacuo*. It was a glass which occurred as a trimer in benzene solution. In the IR spectrum of this compound a poorly structured band between 960 and 1020 $cm^{-1}$ was explained in terms of extensive As-N π bonding. A six-membered ring structure with alternate As and N atoms was assigned to the compound, but the ring conformation could not be determined on IR data alone.

The reaction between $Me_3SiPH_2$ and $(CF_3)_2PI$ or $(CF_3)_2AsI$ to yield $Me_3SiI$

and $(CF_3)_2PPH_2$ or $(CF_3)_2AsPH_2$ has-been reported by Demuth and co-workers [181], but unfortunately they were unable to obtain pure products by fractional distillation since the reactants and products possessed similar boiling points. Accordingly, the products were characterized in the impure state by means of $^1H$, $^{19}F$ and $^{31}P$ NMR spectra. The two compounds $(CF_3)_2PPH_2$ and $(CF_3)_2AsPH_2$ were rapidly oxidized in the air and decomposed at room temperature in the absence of air to give $(CF_3)_2PH$ or $(CF_3)_2AsH$ and a polymeric phosphine.

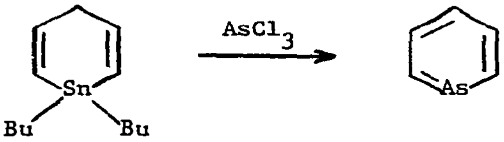
Although compounds of the type RAs=AsR (analogous to the azo compounds) are unknown, Elmes, Leverett, and West [182] have shown that the compound $C_6F_5AsAsC_6F_5$ can exist when bonded to an iron atom to form the complex $Fe(CO)_4(AsC_6F_5)_2$. An X-ray analysis of the complex showed that the arsenic compound was acting as a bidentate ligand. The As-As distance was considerably shorter than the As-As distance found in $(AsMe)_5$ and $(AsPh)_6$. The reactions of $(AsMe)_5$, $(AsEt)_5$, and $(AsPh)_6$ with iron pentacarbonyl and of $(AsMe)_5$ with dimanganese decacarbonyl have also been described [182a].

Although the compound $(Me_2As)_2S_2$ has been known for over 100 years, it had always been assumed to possess the structure $Me_2AsSSAsMe_2$. However, in 1964 Camerman and Trotter [183] established that the compound possessed the structure $Me_2As(S)$-$SAsMe_2$ by means of a single-crystal X-ray analysis. Zingaro and co-workers [184] have now shown by means of PMR and IR studies that the compound in solution exists as an equilibrium mixture of both compounds:

$$Me_2As(S)\text{-}SAsMe_2 \rightleftharpoons Me_2AsSSAsMe_2$$

The relative intensities of the peaks in the PMR were found to vary with the solvent, concentration, temperature, and the time elapsed between preparation of the solution and the PMR measurement. Thus in most cases the spectra showed three peaks; the peaks at δ2.10 and 1.50 ppm were of approximate equal intensity with a third peak at 1.36 ppm which varied widely with the solvent used. The IR spectra of the compound in $CCl_4$ and in $C_2H_2Cl_4$ was found to change as the temperature was raised and this was interpreted as a shift in the equilibrium towards the disulfide form. By the use of the PMR data at several temperatures and concentrations the equilibrium constants, enthalpy changes, entropy changes and the free energy changes for the equilibrium were calculated. A suggested mechanism for the reaction to give the two species was given.

In an extremely valuable paper Ashe [185] reported the preparation and spectral properties of phosphabenzene (phosphorin) and arsabenzene (arsenin). The arsenic compound was prepared from 1,4-dihydro-1,1-dibutylstannabenzene and arsenic trichloride, and the product was isolated by distillation and purified by glpc techniques:



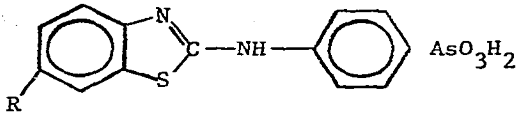
The arsenic compound was an air-sensitive liquid. The PMR spectrum and the mass spectrum were in agreement with the assigned structure. The UV spectrum showed two intense bands at 219 and 268 nm with a shoulder at 305 nm which the author tentatively assigned to an $n \rightarrow \pi^*$ transition.

A three-dimensional X-ray crystal structure study of the 4-membered ring compound $(CF_3As)_4$ has been reported by Mandel and Donohue [186]. The intramolecular distances and angles were given. The ring was slightly distorted from planarity and the As-As-As angles were 83.6°. This distortion was ascribed to relief of Pitzer torsion strain.

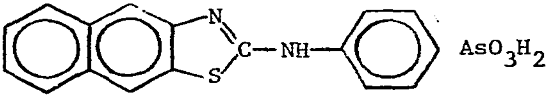
Some reactions of bis(dialkylarsenic)oxides have been reported by Kamai and co-workers [187]. The reaction of bis(diethylarsenic) oxide with PhCOCl gave a mixture of $Et_2AsCl$ and $Et_2AsOCOPh$. Bis(diethylarsenic) oxide reacted with ethyl iodide to give $Et_4AsI$ as well as $Et_2AsH$ and $Et_2AsOEt$. The reaction of bis(diethylarsenic) oxide with methyl iodide gave diethyldimethylarsonium iodide. The reaction of bis(di-*n*-propylarsenic) oxide with methyl iodide gave a product which reacted further with magnesium perchlorate to give dimethyldi-*n*-propylarsonium perchlorate.

## 7. ARSONIC AND ARSINIC ACIDS

A number of arsonic acids (XX and XXI) derived from substituted benzothiazoles and naphthothiazoles have been reported by Panigrahi and co-workers [188].



XX

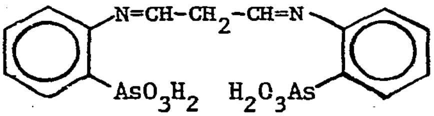


XXI

The compounds showed very little antiamoebic activity against a virulent strain of *Entamoeba histolytica*.

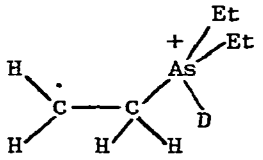
Irgolic, Zingaro and their co-workers at Texas A and M University have developed methods for preparing dialkylarsinic and alkylarsonic acids utilizing the action of Grignard reagents on aminodihalo- and diaminohaloarsines. The straight chain arsonic and arsinic acids were then used to extract metal ions. Because of limited solubility of the long-chain acids the study was extended to the preparation of branched-chain acids [189]. In addition the preparation of di-1-octynylarsinic and 1-octynylarsonic acids were described. The branched-chain acids prepared were bis(2-ethylhexyl)arsinic and bis(1-methylheptyl)arsinic acids and ethylhexylarsonic acid. These three acids were more soluble in organic solvents and were better suited as reagents for metal ion extractions. The acetylenic acids were unstable.

The preparation of the Schiff base arsonic acid from *o*-aminobenzenearsonic

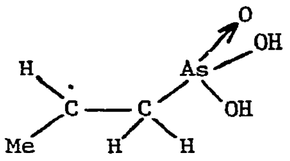


acid and malonaldehyde has been described [190]. The hydrochloride of this acid as well as the disodium salt of the acid formed complexes with Ni, Co, and Cu halides; visible spectra of these complexes were reported.

Lyons and Symons have presented ESR evidence for strong hyperfine interaction between phosphorus, tin, or arsenic atoms β to radical centers [191]. The two arsenic compounds were XXII and XXIII. This coupling was shown to be



XXII



XXIII

due to hyperconjugation rather than due to any involvement of *d*-orbitals of the Sn, P, or As.

The polarographic behaviour of benzenearsonic acid, four substituted benzenearsonic acids and α-naphthalenearsonic acid was determined over the concentration range 5 x $10^{-5}$ M to 1 x $10^{-3}$ M and over the pH range 0-3 [192]. Benzenearsonic acid as well as *o*- and *p*-hydroxybenzene- and 2,4-dihydroxybenzenearsonic acids showed only one reduction wave in solutions of pH < 3. A nitrosubstituted benzenearsonic acid showed an additional wave due to reduction of the nitro group. The half-wave potentials of the various acids were listed, and were all found to be quite similar. This fact, together with the inactivity of phenylphosphonic acid at the dropping mercury electrode, suggested that only the arsenic was being reduced. A mechanism for the reduction involving formation of arsenosobenzene and phenylarsine and their combination to form arsenobenzene was suggested. This mechanism was in part based on thin layer chromatography and the mass spectra of the products produced by macro-scale electrolytic reduction.

The IR spectra and magnetic susceptibilities of complexes formed between uranium(IV) and a variety of arylarsonic acids have been reported by Sandhu and Aulakh [193]. Similar data have also been reported for the cobalt, nickel, and copper salts of benzene- and *o*-aminobenzenearsonic acids by Sandhu and Sandhu [194].

Freedman and co-workers [195] have reported on the molecular weights of a series of phosphonic, phosphinic, arsonic, and arsinic acids in ethanol solution. The apparatus used was a differential isothermal osmometer, and all of the compounds were monomolecular in 95% ethanol.

In continuation of their work on examining the physical properties of long chain dialkylarsinic acids, Smith, Zingaro, and Meyers [196] have reported on the X-ray crystal structure of the acids $R_2AsO_2H$, where R was varied from Me to *n*-$C_8H_{17}$. With the *n*-$C_6H_{13}$, *n*-$C_7H_{15}$ and *n*-$C_8H_{17}$ acids there was a crystal phase change at higher temperatures. It was shown that the cell volumes of the high temperature forms of the *n*-$C_6H_{13}$, *n*-$C_7H_{15}$, and *n*-$C_8H_{17}$ acids were approximately on the same straight line as the Me to Bu acids, when cell volumes were plotted against chain lengths.

A single crystal X-ray analysis of *n*-propanearsonic acid has been reported by Smith, Zingaro, and Meyers [197]. The coordination around the arsenic atom was roughly tetrahedral, and the molecules are linked into "chains of dimers" by hydrogen bonding. Of the three As-O bond distances, one was somewhat shorter than the other two, which was ascribed to the As=O structure.

In continuation of previous work on the effect of arsonic acids on the surface potential and surface tension of aqueous solutions Kamieński and Krauss [198] report on the influence of *o*-, *m*- and *p*-chlorobenzenearsonic acids on the above properties. The surface potentials were plotted against concentrations of the acids to give smooth curves. In the case of *o*-chlorobenzenearsonic acid (0.04 M), the surface potential was determined as a function of the pH of the solution.

A Russian patent [199] covers the preparation of 4-arsono-2'-carboxydiphenylamine by the condensation of *o*-chlorobenzoic acid with arsanilic acid. The reaction was run in alkaline solution in the presence of copper at 120-5°.

An improved method of preparing arsanilic acid by the Béchamp reaction has been patented [200]. The method involved heating aniline and perchloroethylene in the presence of an aqueous solution of Versene, and then adding arsenic acid.

1-(*o*-Arsonophenylaxo)-2-naphthol and the "*o*-arsonanil" of 2-hydroxy-1-naphthaldehyde have been recommended as reagents for the determination of scandium [201], A number of other papers have appeared in which arsonic acids have been used in analytical chemistry, particularly in the determination of metal ions. Most of these compounds belonged to the class of arsonic acid-substituted azo compounds (Arsenazo). A new Arsenazo type reagent, considerably more sensitive than Arsenazo, was introduced by Basargin and co-workers [202]. It was termed Arsenazokhimda. The fluorescent spectra of various metal ions complexed with two different Schiff bases containing arsonic acid groups have been reported by Holzbecher and Volka [203]. Another paper on the infrared spectra of the complexes of various metals with Arsenazo I and Thoron I has been published by Pilipenko and Shevchenko [204]. The stability constants of the compounds formed between alkaline earth metals and a variety of *o*-arsono-*o*'-hydroxyazo compounds have been determined by Kina and Toei [205].

## 8. TERTIARY ARSINE OXIDES AND RELATED COMPOUNDS

Triphenylarsine oxide was shown to react with butyl iodide in acetone solution with the reversible formation of butoxytriphenylarsonium iodide [206]. The latter compound then reacted further with triphenylarsine oxide to yield $Ph_3As(OH)OAs(I)Ph_3$ and 1-butene. By means of conductivity measurements the rate of formation of the intermediate butoxy compound was determined. It was concluded that this intermediate product was probably too labile to be isolated.

Usacheva and Kamai [207] had previously reported that reaction between acetyl bromide and triphenylarsine sulfide yielded the following products:

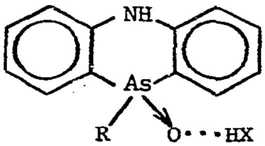
$$MeCOBr + Ph_3AsS \longrightarrow EtBr + Ph_2AsCOMe + Ph_2AsBr + MeCOSEt$$

The present paper [208] is a further investigation of this reaction in which both the reaction time and the ratios of the reactants were varied. On the basis of these results a mechanism for the reaction was suggested.

Triphenylarsine oxide (1 mole) reacted with two moles of acetyl bromide in toluene solution to give triphenylarsenic dibromide in 87.2% yield [209]. The dibromide was readily hydrolyzed to $Ph_3As(OH)Br$. The IR spectra of both the dibromide and hydroxybromide were given.

10-Alkyl-5,10-dihydrophenarsazine 10-oxides have been shown to react with hydriodic acid with the cleavage of RI and the formation of 10-iodo-5,10-dihydrophenarsazine [210]. In contrast, 10-phenyl-5,10-dihydrophenarsazine 10-oxide was cleaved by hydriodic acid to give diphenylamine. Both 10-alkyl- and 10-phenyl-5,10-dihydrophenarsazine 10,10-diiodides reacted with iodine to give 10-iodo-5,10-dihydrophenarsazine. An $S_N2$ mechanism involving an attack of $I^-$ on the 10-alkyl group was suggested for the reactions of the 10-alkyl compounds. It was also shown that 10-ethyl-5,10-dihydrophenarsazine reacted with ethyldibromoarsine to form 10-bromo-5,10-dihydrophenarsazine.

Gavrilov and co-workers [211] have reported the basic properties of 10-alkyl- and 10-aryl-5,10-dihydrophenarsazine 10-oxides. They appeared to be somewhat weaker bases than triphenylarsine oxide. A number of adducts of the phenarsazine 10-oxides with HCl, HBr, trichloroacetic acid, and pentachlorophenol were listed. These compounds were believed to be hydrogen bonded adducts of the general formula XXIV:



XXIV

It was also demonstrated that 10-alkyl- and 10-aryl-5,10-dihydrophenarsazine

10-oxides in a mixture of acetic acid and acetic anhydride could be titrated with perchloric acid. The change in potential occurred with a ratio of acid to substrate of 1:1. Since under the same conditions 10-isopropyl-5,10-dihydrophenarsazine could not be titrated with perchloric acid, it was concluded that the As=O grouping was protonated rather than the nitrogen.

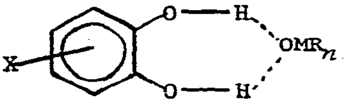
The authors [212] then prepared a series of arsinous acid esters with different hydrocarbon groups serving as the ester function. These esters were then allowed to react with alkyl halides to form arsonium salts. In no case was the alkyl group of the ester found in the arsonium salt:

$$RR'AsOR'' + RI \longrightarrow [R_3R'As]\,I$$

For example esters of the type $Et_2AsOR$, where R = Me, Et, Ph, *t*-Bu, or benzyl, all reacted with ethyl iodide to give tetraethylarsonium iodide. Similar results were obtained with $Pr_2AsOR$ and EtPhAsOR. The results of these experiments on the mechanism of the reaction were discussed.

Since alkoxyphosphonium salts (containing at least one alkoxy group attached to the phosphorus) are stable compounds, Kamai, Chernokal'skii, and Moisak [213] attempted the preparation of similar arsonium salts. The reaction of triphenylarsenic dibromide with sodium butoxide in butyl alcohol gave only the crystalline salt-like compound $Ph_3AsO{\cdot}HBr$. The reaction of $Ph_3AsBr_2$ with one mole of sodium perchlorate in acetone solution gave a precipitate of sodium bromide, but addition of sodium butoxide (or of sodium ethoxide) gave only the compound $2Ph_3AsO{\cdot}HClO_4$. An attempt to alkylate triphenylarsine oxide with triethyloxonium tetrafluoroborate gave only the addition product $Ph_3AsO{\cdot}BF_3$. A second attempt to alkylate triphenylarsine oxide with dimethyl sulfate in the presence of perchlorate ion again led to the formation of $2Ph_3AsO{\cdot}HClO_4$.

Davenport and co-workers [214] have shown that hydrogen-bonded adducts of the type XXV (where M = N, P, or As and *n* = 3, or M = S and *n* = 2) can be formed



XXV

either by reaction of the oxides $R_nMO$ with catechol or, in the case where M = P or As, by hydrolysis of the adducts formed from triphenylphosphine or triphenylarsine with catechols. The hydrogen bonded adducts were surprisingly stable and could often be sublimed without decomposition. The authors reported a preliminary X-ray crystal structure of the adduct formed from tetrachlorocatechol and triphenylarsine oxide. In a later paper [215] the complete X-ray data for this complex were reported.

The electrochemical reduction of a series of arsine oxides at the dropping mercury electrode in dimethylformamide solution has been studied by Kargin and co-workers [216]. The arsine oxides were $Ph_3AsO$, $PhEt_2AsO$, ($p$-$MeC_6H_4$)-$n$-$Pr_2AsO$, and a series of phenyl substituted compounds of the type $p$-$RC_6H_4Et_2AsO$. All of the oxides were reduced in an irreversible two-electron step, except for the $p$-Cl and $p$-$BrC_6H_4Et_2AsO$ derivatives where two waves of equal height were observed, one of which was believed due to reduction of the C-halogen bond. When the reduction was carried out in the presence of phenol, a much more complicated reduction occurred involving a transfer of four electrons per mole. The reduction was believed to occur by cleavage of the Ar-As bond and protonation of the aryl anion.

In order to evaluate the electron-acceptor capacity of arsenic containing groups the authors [216] studied the half-wave potentials of a series of *m*- and *p*-substituted nitrobenzenes in which two of the substituents were $p$-$As(O)Et_2$ and $p$-$AsEt_2$. By plotting the Hammett $\sigma$ constants for the various stustituents *vs.* the half-wave potentials of the compounds, values of $\sigma$ for $p$-$As(O)Et_2$ (+0.33) and $p$-$AsEt_2$ (0.09) were obtained. The electrophilic constants, $\sigma^+$ were +0.39 and ∿ −0.02 for the same two substituents. It was suggested that there was some

$p_\pi - d_\pi$ interaction between the arsenic atom and the π-system of the benzene rings.

The infrared and Raman spectra of the compounds $Me_3MO$, where M is N, P, or As have been reported by Choplin and Kaufmann [217]. A normal coordinate analysis resulted in the assignment of the frequencies and a calculation of the force constants. Bond orders were calculated using formulas developed by Gordy and by Siebert. It was suggested that there was considerable $p_\pi - d_\pi$ interaction in the case of the phosphorus and arsenic compounds.

Bravo and co-workers [218] have compared the molar magnetic rotations of the adducts $R_3PO{\cdot}BF_3$ and $R_3AsO{\cdot}BF_3$, where R = Et, Pr, or Bu, with the rotations of the corresponding uncoordinated phosphine and arsine oxides and noted a marked diminution in rotation for the coordinated species. This effect is brought about by changes in the bond between the hetero atom (P or As) and the oxygen. The increase in molar rotation for each $CH_2$ group was calculated.

The infrared and Raman spectra of the two molecular complexes $SbCl_3{\cdot}2Ph_3AsO$ and $BiCl_3{\cdot}2Ph_3AsO$ have been reported by Miličev and Hadži [219]. A number of the vibrational bands were assigned.

The use of reversed-phase extraction chromatography on silica gel layers impregnated with tri-*n*-octylarsine oxide for the separation of a wide variety of inorganic ions was described [220]. $R_f$ data for 30 ions as a function of $Cl^-$ concentration in HCl or in HCl–LiCl eluents were given.

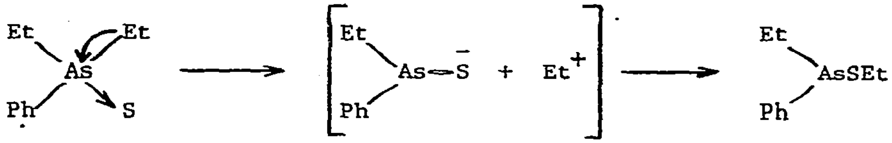
Triphenylarsine oxide has been found to be a corrosion inhibitor in studies of the corrosion of "carbonyl iron powder" in hydrochloric acid [221].

A number of papers have appeared in which trialkyl- or triarylarsine oxides have served as donor ligands to the following metals: cobalt [222], copper [222], indium [223], iron [222, 224], manganese [222], magnesium [222], mercury [122a], nickel [222, 225], uranium [226–228], and zinc [222].

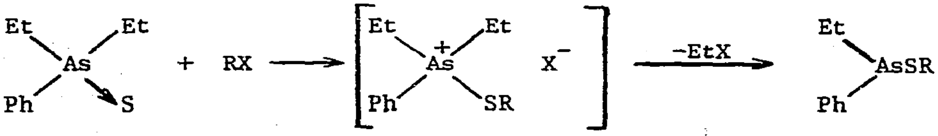
Moreland and co-workers [229] studied $^1$H and $^{19}$F NMR spectra of tribenzylarsenic difluoride as a function of temperature. At 0° the methylene protons occurred as a triplet which coalesced to a broad singlet and finally to a sharp singlet as the temperature was raised to 45°. This result indicated that an intermolecular exchange of fluorines must occur with increase in temperature. This fluoride exchange was shown to be first order in the difluoride, *i.e.*, the lifetime was independent of concentration. Since the compound was monomeric the mechanism of exchange was believed to involve a dissociative step. The energy of activation was found to be 12.3 ± 2.0 kcal/mole.

Previous spectroscopic studies [230] had suggested that trimethylarsenic dichloride contained pentacovalent arsenic whereas trimethylarsenic dibromide was ionic with a tetrahedral arsenic atom. A preliminary communication on the X-ray analysis of these two compounds was in agreement with the earlier spectroscopic studies [231].

The isomerization of dialkylarylarsine sulfides at 200° to alkyl alkylarylthioarsinites has been the subject of previous investigations [232]. Gatilov and Kovyrzina [233] have now used differential thermal analysis as a method of investigating the mechanism of the reaction. They concluded that there was a heterolytic cleavage of the sulfide to give an ionic intermediate which subsequently reacted to form the final product:



They also demonstrated that addition of an alkyl halide greatly facilitated the isomerization. This effect was attributed to the intermediate formation of an arsonium salt:



A similar study of triethylarsine sulfide by means of differential thermal analysis gave similar results [234]. The rearrangement of triethylarsine sulfide in the presence of *n*-butyl bromide was also studied.

A preliminary communication, with very little information about the compounds prepared, mentioned the use of tertiary phosphine sulfides and selenides and one tertiary arsine sulfide ($Me_3AsS$) as ligands to chrominum and tungsten carbonyls [235].

In contrast to triarylarsine sulfides which react with alkyl iodides to give sulfur-free products, trialkylarsine sulfides react with alkyl iodides to give (alkylthio)arsonium salts [236]:

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

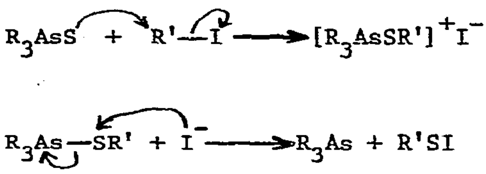
The structure was based only on elemental analysis and no spectral data were given. It was also found that both trialkyl- and triarylarsine sulfides reacted with trialkyloxonium tetrafluoroborates to give the (alkylthio)arsonium tetrafluoroborates:

$$Ph_3AsS + R_3OBF_4 \longrightarrow [Ph_3AsR]BF_4 + R_2O$$

Further work on the mechanism of this reaction indicated that with triarylarsine sulfides, triarylarsines are intermediates in the reaction [237]:

$$Ar_3AsS + RI \longrightarrow Ar_3As \xrightarrow{RI} Ar_3R\overset{+}{As}I^-$$

If tri-*p*-tolylarsine sulfide was allowed to react with methyl iodide for three days, only methyltri-*p*-tolylarsonium iodide was obtained; but with the less reactive ethyl iodide, after 12 days a 38.2% yield of tri-*p*-tolylarsine was obtained. It was also shown that trialkylarsine sulfides and alkyl iodides gave tetraalkylarsonium iodides rather than trialkyl(alkylthio)arsonium salts, when the reaction mixture was heated. In the light of these results the authors [237] have proposed the following mechanism:



$$R_3AsS + R'{-}I \longrightarrow [R_3AsSR']^+I^-$$

$$R_3As{-}SR' + I^- \longrightarrow R_3As + R'SI$$

They then attempted to isolate dialkyl sulfides from the reaction mixture; these should arise by disproportionation:

$$2R'SI \longrightarrow R'SSR' + I_2$$

And while they were unable to isolate any disulfides from the reaction mixture, they did succeed in obtaining the products expected from the reaction of mercuric chloride with disulfides, namely, $EtSHgCl{\cdot}HgCl_2$ and EtSHgCl. These were obtained by adding $HgCl_2$ to the reaction mixture from triethylarsine sulfide and ethyl iodide. They were also able to obtain a positive nitroprusside test after the addition of KCN solution and sodium nitroprusside.

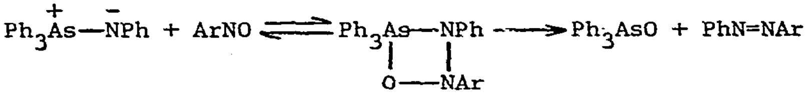
In continuation of previous work on arsine imides Frøyen [238] has demonstrated that under mild conditions phenyl isocyanate reacts with triphenylarsine oxide to form triphenylarsine phenylimide:

$$PhN{=}C{=}O + Ph_3AsO \longrightarrow Ph_3As{=}NPh + CO_2$$

Previous reports that only diphenyl carbodiimides were found in this reaction were due to the more vigorous reaction conditions employed. Frøyen has shown that if the arsine imide was heated with phenyl isocyanate in dry benzene, diphenyl carbodiimide was indeed the product of the reaction. In addition to phenyl isocyanate, arsine imides were obtained from *p*-toluenesulfonyl isocyanate, diphenylphosphinyl isocyanate, and α-naphthyl isocyanate.

The author [238] also found that N-sulfinyl derivatives of amides reacted with triphenylarsine oxide to give the corresponding arsine imides and sulfur dioxide. By contrast, N-sulfinylaniline gave only an addition product with essentially no evolution of sulfur dioxide, whereas N-sulfinyl-*p*-nitroaniline gave the arsine imide and sulfur dioxide. The importance of an electron-attracting group attached to the -N=S-O was considered in respect to the mechanism of the reaction.

In contrast to phosphine imides, which do not react with nitroso compounds, triphenylarsine phenylimide was shown to react with nitrosobenzenes to give azobenzene derivatives in excellent yields [239]. The reaction was believed to follow a mechanism similar to the Wittig reaction:



## 9. ARSONIUM COMPOUNDS AND ARSENIC YLIDS

The reaction between triphenylarsine and iodine has been the subject of many papers. Espeillac and Decroocq [240] now report a study of this reaction in a variety of solvents. The course of the reaction was followed spectrophotometrically with the use of the Beckman DU Spectrophotometer. Dielectric constant measurements and conductometric measurements were also employed. In non-polar solvents a 1:1 complex, $Ph_3As\cdot I_2$, which has considerable ionic character was formed. In more polar solvents a 1:2 complex $Ph_3As\cdot 2I_2$ can also be formed. The dissociation constant for the reactions

$$Ph_3AsI_2 \rightleftharpoons Ph_3AsI^+ \ I^-$$

and

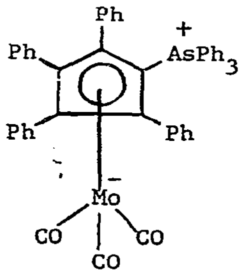
$$Ph_3As\cdot 2I_2 \rightleftharpoons Ph_3AsI^+ \ I_3^-$$

was determined in various solvents.

In continuation of previous work on the reaction between onium salts and alkali metal tetraalkylaluminates, Gavrilenko and co-workers [241] have prepared a series of phosphonium, arsonium, and stibonium complexes. Two arsenic compounds $[Me_4As][AlEt_4]$ and $[Et_4As][AlEt_4]$ were obtained from $Me_4AsI$ or $Et_4AsI$ and $NaAlEt_4$. The reactions were run in toluene solution and were catalyzed by triethylaluminum. Tetramethylarsonium iodide also reacted with triethylaluminum to give $[Me_4As][AlEt_3I]$. This latter complex also reacted with sodium tetraethylaluminate to yield $[Me_4As][AlEt_4]$ and $Na[AlEt_3I]$. Reduction of $[Me_4As][AlEt_4$ or $[Et_4As][AlEt_4]$ with $LiAlH_4$ gave the interesting compounds $[Me_4As][AlH_4]$ and $[Et_4As][AlH_4]$. When $LiAlD_4$ was used the deuterated analog $[Me_4As][AlD_4]$ was obtained. The reaction of $[Et_4As][AlEt_4]$ with $LiBH_4$ led to the compound $[Et_4As][BH_4]$. The thermal decomposition of the complexes was also studied, but few details of these pyrolyses were given.

In a preliminary communication Schipper and Buck [242] report on the PMR spectra of a series of norbornadiene compounds substituted in the 7-position by such charged groups as $^+AsPh_3$, $^+SbPh_3$, $^+BiPh_3$, etc. The coupling constants for the various proton-proton interactions were reported, and it was concluded that there must be direct interaction between the positively-charged center and the double bond.

In a paper devoted mainly to coordination compounds formed by triphenylphosphonium cyclopentadienylide, the compound XXVI was prepared [243] and its infrared spectrum reported.



XXVI

In a paper devoted to the nature of ambident ions Austad and co-workers [244] have studied the reaction of trityl chloride or trityl perchlorate with tetraphenylarsonium cyanide in acetonitrile to obtain a mixture of trityl isocyanide and trityl cyanide.

In a study of anionic species formed in the hydrolysis of a number of trivalent and pentavalent trifluoromethylphosphorus compounds, the two arsonium salts $[Ph_4As][CF_3PSO_2H]$ and $[Ph_4As][CF_3PS_2OH]$ have been isolated and characterized [245].

The PMR spectra of a variety of alkyl- and alkylarylarsonium salts have been studied by Zykova and co-workers [246]. One group of compounds studied was $Et_nPh_{4-n}As^+$, where $n$ was varied from 1 to 4. The chemical shifts of the methylene protons of the ethyl group were found to shift to lower fields (increase in $\delta$ values) with an increase in the number of phenyl groups. Thus values of $\delta$ (in ppm) for the four compounds where $n$ varied from 1 to 4 were 3.55, 3.30, 2.98, and 2.65, respectively, with a constant increment of about 0.3 ppm for each phenyl group. A similar effect was found for the methyl protons of the three compounds $Me_nPh_{4-n}As^+$, where $n = 1, 3,$ or 4. The effect was attributed to an increase in the positive charge on the arsenic with an increase in the number of phenyl groups resulting in a decreased screening of the methylene protons.

In addition to the substituted compounds mentioned above, the PMR spectra of the symmetrical compounds $Et_4AsX$ were studied and the chemical shifts of the methylene protons were found to vary with the concentration of the solution, the nature of the solvent, and to some extent with the nature of the anion. The change in $\delta$ values with concentration, the authors suggest, might be attributed to an increase in ionization of the pentacovalent arsenic species or to dissociation of an ion pair:

$$Et_4AsI \rightleftharpoons Et_4As^+I^- \rightleftharpoons Et_4As^+ + I^-$$

In a study of the solvation of several onium salts by Jolicoeur and co-workers [247], tetraphenylarsonium chloride was one of the onium salts investigated.

A PMR study of the interaction of tetraphenylphosphonium, tetraphenylarsonium, and tetraphenylborate ions with water, ethanol, and methanol has been made by Coetzee and Sharpe [248]. They concluded that these ions undergo a wide variety of solvation effects. A study of ion pairing in aqueous solutions of tetraalkylarsonium chloride, iodide, and hydroxide has been made by Larsen [249]. PMR techniques were used in this study.

A paper devoted to the Raman spectra of a number of phosphonium, arsonium, and stibonium salts has been published by Orenberg and co-workers [250]. The major portion of the paper was devoted to antimony compounds and is discussed in the Antimony section. The three arsenic compounds $Ph_4AsCl$, $(Ph_4As)_2SO_4$, and $Ph_4AsF$ gave identical spectra except for differences attributable to the anion, and all three compounds appeared to be ionic and contain tetravalent arsenic in the solid state. The Raman spectra of $Ph_4AsCl$ (and of $Ph_4SbCl$) in aqueous solution was given for the X-sensitive region of the spectra. The assignment of structures to the various compounds investigated was based largely on the spectra obtained in the X-sensitive region.

Both the powder pattern X-ray analyses and the IR spectra of tetraphenylphosphonium and arsonium permanganates and perchlorates have been reported by Baran [251]. It was concluded that the large tetraphenylarsonium or phosphonium cation had little or no influence on the spectrum of the anion. In a similar manner, based on X-ray diffraction and IR studies, Walford and co-workers [252] have concluded that with the salts $Ph_4AsBF_4$, $Ph_4AsPF_6$, $Ph_4AsAsF_6$ and $Ph_4AsSbF_6$ the anion has little effect on the spectrum of the cation.

The partial molal volume of tetraphenylarsonium tetraphenylborate at infinite dilution in aqueous solution has been calculated by Millero [253]. The apparent molal volumes of tetraphenylarsonium chloride in water were determined at temperatures of 0, 25 and 50° by this same author [254].

A theoretical discussion of the catalytic activity of various onium compounds in the liquid-phase oxidation of hydrocarbons has been given by Ohkubo [255]. The relatively low activity of arsonium and telluronium compounds was ascribed to the vacant and diffused *4d* and *5d* orbitals in such compounds.

In continuation of earlier work on phase transitions of anion radical salts containing mixed cations, Iida [256] has investigated the transition temperature and the magnitude of the heat of the transition as a function of the composition parameter x, for the compounds $(Ph_3PMe)_{1-x}^{+} (Ph_3AsMe)_x^{+} (TCNQ)_2^{-}$ where $0 \leq x \leq 1$.

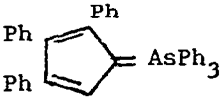
Tsentovskii and co-workers [257] have studied the conductivities of a series of arsonium salts, $R_4AsX$, where R was alkyl or arylalkyl and X was I, Br, or $ClO_4$ in acetone, nitromethane, and dimethylformamide. With the exception of tetrapropylarsonium and diethyldiphenylarsonium iodides in dimethylformamide, all of the salts studied were found to be weakly associated electrolytes in the solvents investigated.

The crystal structures of methyltriphenylarsonium and methyltriphenylphosphonium bis(α,α,α',α'-tetracyanoquinodimethanides) have been reported in a paper by McPhail, Semeniuk and Chesnut [258].

Tetraphenylarsonium chloride has been used as a titrant in the determination of the perbromate ion by potentiometric titration [259]. Triphenylmethylarsonium chloride has been used in the preparation of polyesters derived from bivalent halogenated phenols [260]. A German patent [261] claims the use of $[Ph_4As][BPh_4]$ as a hardening promoter in the preparation of epoxy resins.

A number of papers have appeared in which tetraaryl- or tetraalkylarsonium salts of metals or metal complexes have been isolated. Often the salts were involved in the analytical determination of the metals. Among arsonium salts of metals or metal complexes isolated were there of cobalt [262, 263], gallium [264], iron [265], indium [262], niobium [266], silver [267], tantalum [268], tellurium [269], thallium [262], tin [119], vanadium [270, 271] and zinc [263].

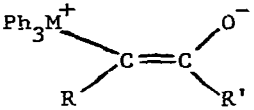
Although diazotetraphenylcyclopentadiene reacts with triarylphosphines, -arsines, -stibines, and similar compounds to give ylids, diazo-2,3,4-triphenylcyclopentadiene failed to undergo a similar reaction [272]. Accordingly, alternate methods were found to obtain several pyridinium, phosphonium and arsonium ylids. The ylid XXVII was obtained from 1,2,3-triphenylcyclopentadiene



XXVII

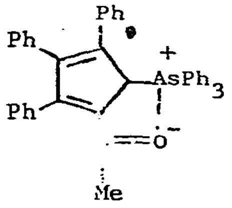
and $Ph_3AsO$ by refluxing in triethylamine in the presence of $P_2O_5$ for 24 hrs. If acetic anhydride was used as the solvent, the H atom on the cyclopentadiene ring was replaced by an acetyl group. Both of these arsonium ylids formed crystalline salts on treatment with perchloric acid.

Dale and Frøyen [273] have reported on the PMR spectra of a series of arsenic and phosphorus ylids of the types $p$-$XC_6H_4M{=}C(R)COR'$ and $p$-$XC_6H_4M{=}C(R)COOR'$, where M = As or P, and concluded that the β-keto-stabilized ylids, in contrast to the ester-stabilized ylids, did not undergo rotation about the enolate C=C bond with the formation of *cis-trans* isomers. This conclusion was based upon the failure of the PMR spectra to show temperature dependence. The authors concluded that the *cis* isomer predominated, and that this was due to attraction between the positive hetero atom (P or As) and the negative keto oxygen:



A kinetic study of the reaction of a series of stabilized arsonium ylids $Ar_3As{=}CHCOX$ (where Ar = Ph, $p$-$MeOC_6H_4$, or $p$-$MeC_6H_4$ and X is a wide variety of groups including Me, Ph, substituted phenyl, OMe, and $NPh_2$) with $p$-nitrobenzaldehyde was carried out [274]. In general it was found that the more reactive ylids were more basic, a conclusion similar to results obtained with phosphorus ylids in the Wittig reaction. A Hammet plot of the rate constants *vs*. the σ values for the $p$-substituted ylids, $Ar_3As{=}CHC_6H_4X$-$p$, gave a straight line with a ρ value of −2.2. It was shown that rates of reactions were five times faster in benzene than in dimethylformamide and two times faster in benzene than in dimethyl sulphoxide. This result (that the reaction proceeds faster in the non-polar solvent) is not consistent with the usually accepted mechanism of the reaction in which a betaine is formed as the first step of the reaction.

The C=O stretching frequency (1565 $cm^{-1}$) in 2-acetyl-3,4,5-triphenylcyclopentadienylide was considerably lower than expected, which suggested bonding between the oxygen and arsenic as in XXVIII [275]:



XXVIII

Ferguson and co-workers have published a preliminary report on the single crystal X-ray study of this compound which confirmed the bonding between the As and O atoms. Thus the As–O distance was considerably shorter than the sum of the appropriate van der Waals radii but longer than a typical As–O distance. The As–C distances were also longer than normal. The molecule thus appears to contain a trigonal bipyramidal arsenic atom with an oxygen and one phenyl group in apical positions.

Having studied the reaction of phosphorus ylids of the type $Ph_3P{=}CHCO_2R$ with $N_2F_4$, Fokin and co-workers [276] have extended this reaction to the corresponding arsenic ylid. The main reaction product from $N_2F_4$ and $Ph_3As{=}CHCO_2Et$ was a crystalline solid to which the authors assigned the structure $Ph_3As(F)CHFCO_2Et$ (based on elementary analysis). This can react further with $N_2F_4$ to produce $CHF_2CO_2Et$. The $Ph_3As(F)CHFCO_2Et$ was hydrolyzed under fairly severe conditions to yield $Ph_3AsO$ and $CH_2FCO_2Et$.

Arsenic ylids of the type $Ph_3As{=}CH_2$ and $Ph_3As{=}CHPh$ are unstable and react with carbonyl compounds to give both the normal Wittig reaction products as well as triphenylarsine and an epoxide. By contrast, arsenic ylids of the type

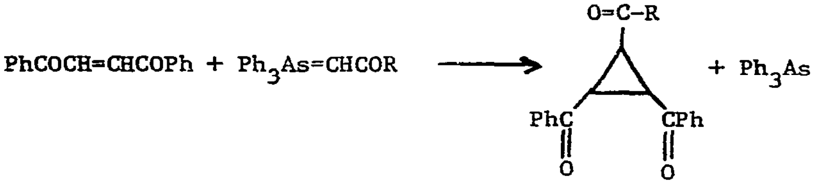
$Ph_3As$=CHCOR are stable and give only the Wittig reaction products with carbonyl compounds. Nesmeyanov and co-workers [277] have now studied the kinetics of the reaction between the stable arsenic ylids and substituted benzaldehydes, and compared these rate constants with those obtained from some of the corresponding phosphorus ylids. They concluded that the mechanism of the Wittig reaction for phosphorus ylids and the stable arsenic ylids was the same. The arsenic ylids, however, reacted several hundred times more rapidly than the corresponding phosphorus ylids. Because arsenic ylids also reacted with some carbonyl compounds which do not react with phosphorus ylids, the arsenic ylids, when applicable, have an advantage for the Wittig reaction.

The PMR spectrum of the arsonium ylid, triphenylarsonium cyclopentadienylide, has been reported by Ernstbrunner and Lloyd [278] and compared with the PMR spectra of the corresponding phosphonium ylid and with dimethylsulfonium cyclopentadienylide. The spectrum of the arsonium compound indicated that there was more delocalization (more cyclopentadienide character) than with the phosphours and sulfur compounds.

Several workers have previously demonstrated that phosphonium ylids of the type $Ph_3As$=CRCOOR' existed in *cis* and *trans* forms at low temperatures. Dale and Frøyen [279] have now extended this concept to the corresponding arsonium ylids. The investigation of *cis-trans* isomerism was carried out by means of PMR studies which clearly showed the existence of the two isomers at low temperatures. The three compounds used were $Ph_3As$=CRCOOMe, where R=H, Ph, or CN. It was found, as in the case of the phosphonium ylids, that the *cis* isomer predominated, but that the *cis/trans* ratio was larger for phosphorus than for arsenic compounds. The free energy of activation for the *cis* $\rightleftarrows$ *trans* conversion was shown to increase in the order R=H, Ph, CN.

The ylid, triphenylarsonium cyclopentadienylide, which had not previously been successfully prepared, has not been synthesized by Freeman and Lloyd [280]. The preparation involved the reaction of the dibromocyclopentene (formed by the bromination of cyclopentadiene) with triphenylarsine to form a bisarsonium salt, which yielded the desired ylid on treatment with alkali. The tri-*p*-tolyl- and tris(*p*-methoxyphenyl)arsonium ylids were prepared in a similar manner. The triphenyl ylid coupled with benzene-diazonium chloride to yield a colored azo compound. The triphenyl ylid reacted with benzaldehyde, *p*-nitrobenzaldehyde, and cinnamaldehyde to give principally triphenylarsine oxide and small amounts of triphenylarsine, but the other products of the reaction have not as yet been identified.

Nesmeyanov and Mikul'shina [281] have studied the reaction of arsenic ylids of the type $Ph_3As{=}CHCOR$ (R = Ph, Me, or OMe) with *trans*-dibenzoylethylene and with dimethylfumarate. The products in each case were triphenylarsine and derivatives of cyclopropane:

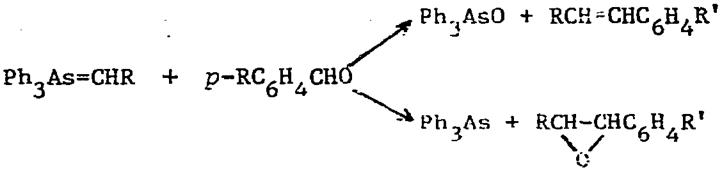


XXIX

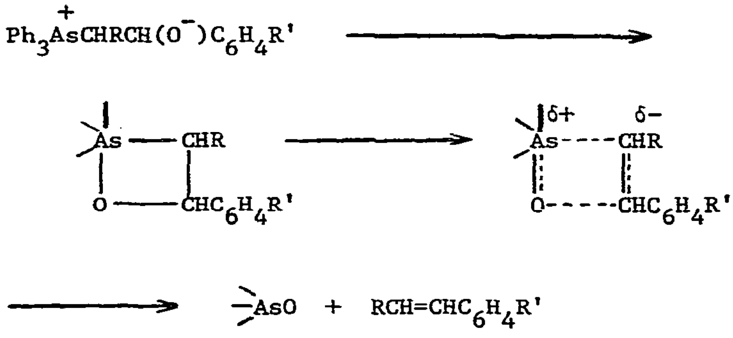
It was also shown that the ylid $Ph_3As{=}CHCOR$ in benzene solution decomposed slowly when allowed to stand in diffused light to give $Ph_3As$ and XXIX (R = Ph). A mechanism for this reaction, which involved the photochemical splitting of the ylid to form triphenylarsine and a carbene as the initial slow step, was postulated:

$$Ph_3As{=}CHCOPh \xrightarrow[\text{slow}]{h\nu} Ph_3As + [:CHCOPh]$$

Many previous investigators have shown that the reaction of arsenic ylids with aldehydes or ketones led to the formation of either olefins and arsine oxides or to epoxides and arsines. In an attempt to find the factors which influenced the course of the reaction, Trippet and Walker [282] have studied the reactions of substituted benzylidenetriarylarsoranes ($Ph_3As{=}CHR$) with *p*-substituted benzaldehydes:



When the substituent R in the ylid was a strong electron-attracting group, $NO_2$, CN, or $CO_2Et$, regardless of the nature of the group R' on the aldehyde, the olefin was formed exclusively. This was explained as due to the ability of the group R to stabilize an adjacent carbanion and by the assumption that in the transition state, XXX, the As-C bond breaks in advance of other electron shifts:



XXX

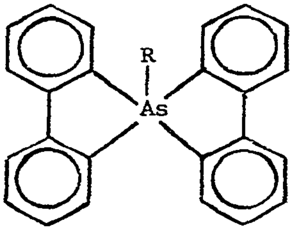
Where R was Ph or *p*-$ClC_6H_4$, only the epoxide was formed.

Methylenetriphenylarsorane reacted with α,β-unsaturated ketones to give cyclopropane derivatives. Benzylidenetriphenylarsoranes and Schiff bases gave aziridines. In this case the arsoranes resembled sulfur ylids rather than phosphorus ylids. Other reactions investigated included the reaction of the arsoranes with dimethyl acetylenedicarboxylate, and with benzensulfinyl and benzenesulfonyl chlorides.

The reaction of the arsonium ylids $CH_2=AsPh_3$ and $CH_3CH=AsPh_3$ with a series of *o*-aminoaryl ketones to form 3-substituted indoles has been the subject of a communication by Bravo and co-workers [283]. The reaction proceeded in a similar manner to that observed with dimethylsulfonium and dimethyloxosulfonium methylides, as described in earlier publications by the same authors. The yields of indoles obtained varied from large (98%) to medium.

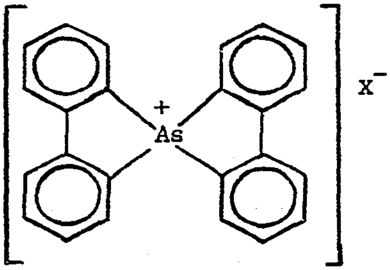
## 10. MISCELLANEOUS

In a detailed paper Hellwinkel and Knabe [284] have discussed the preparation and reactions of alkyl- and alkenylbis(2,2'-biphenylene)arsenic compounds XXXI.



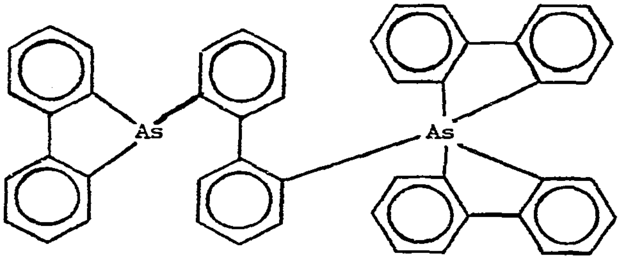
XXXI

The isopropyl compound (XXXI, R = $Me_2CH$) was readily prepared from XXXII and isopropylmagnesium chloride in ether solution, but where R = cyclopentyl, THF was necessary to effect the reaction. Where R = *t*-Bu, the Grignard reaction



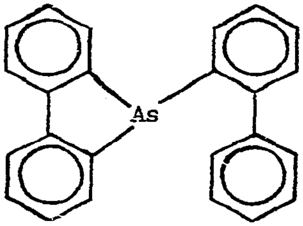
XXXII

gave the dimer XXXIII, but the desired XXXI (R = *t*-Bu) could be obtained from *t*-butyllithium and the arsonium salt XXXII.



XXXIII

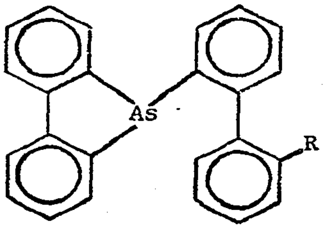
The compound XXXI (R = *t*-Bu) was unstable and decomposed at room temperature to the tertiary arsine XXXIV and isobutylene.



XXXIV

This same product (XXXIV) was obtained when the spirane was treated with HCl in THF.

When XXXII was allowed to react with neopentylmagnesium bromide, a product was obtained which gave a molecular weight (by mass spectroscopy) corresponding to XXXI (R = neopentyl) but which showed all the properties of a tertiary arsine. On the basis of the fragmentation pattern obtained in the mass spectrometer, it was concluded that the compound possessed the structure XXXV (R = $CH_2CMe_3$).

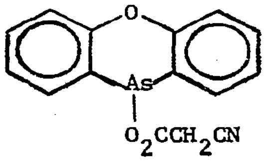


XXXV

This compound was then synthesized by a different and unequivocal route. The reaction of 2-methyl-2-phenylpropylmagnesium chloride with XXXII in ether or THF gave a compound XXXV (R = $CH_2C(Ph)Me_2$). When the three derivatives of XXXI (R = *i*-Pr, cyclopentyl, or *t*-Bu) were heated 30-50° above their melting points, XXXIV and the corresponding olefins (propene, cyclopentene, or isobutylene) were obtained by β-elimination. The course of the reaction was followed by the use of the deuterium labelled compound XXXI (R = $CD_2Me$), wherein it was shown that all of the deuterium occurred in the ethylene formed by the thermolysis.

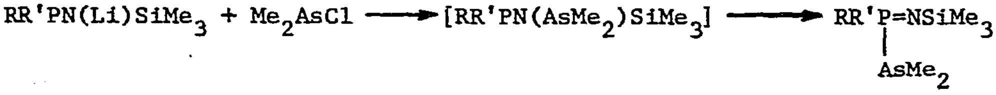
In addition to the alkyl derivatives of XXXI, the two styryl derivatives of XXXI (R = *cis*-CH=CHPh and *trans*-CH=CHPh) were prepared from the corresponding Grignard reagents. Thermolysis of these compounds did not give phenylacetylene by β-elimination as expected, but rather XXXV (R = *cis*-styryl and R = *trans*-styryl, respectively). Thermolysis of the vinyl compound XXXI (R = $CH=CH_2$) gave a mixture of acetylene, XXXIV, and the rearrangement product XXXV (R = $CH=CH_2$). The authors also investigated the cleavage of the compounds XXXI (R = Me, Et, or $PhCH_2$) with boiling alcohol. In each case XXXIV was obtained. The mechanism of this reaction was followed by means of deuterium-labelled ethanol.

The compound XXXVI was obtained from 10,10'-oxydiphenoxarsine by treatment with cyanoacetic acid [285]. It was prepared for use as a pesticide.



XXXVI

In a paper devoted largely to phosphazenes, the arsenic-containing compound $(Me_3C)MeP(AsMe_2)=NSiMe_3$ was prepared by the reaction of $(Me_3C)MePN(Li)SiMe_3$ with dimethylchloroarsine [286]:



$$RR'PN(Li)SiMe_3 + Me_2AsCl \longrightarrow [RR'PN(AsMe_2)SiMe_3] \longrightarrow RR'\underset{\underset{AsMe_2}{|}}{P}=NSiMe_3$$

The NMR spectra of the compounds prepared were listed and gave evidence for the structural assignments.

An analytical method for the determination of tertiary arsines by titration with iodine in aqueous acetic acid without previous destruction of organic matter has been suggested by Sandhu and co-workers [287]. The end point was determined either potentiometrically or with the use of starch as an indicator. A spectrophotometric procedure for the determination of arsenic in organic arsenicals which involved the destruction of organic matter and conversion of arsenic to arsine has appeared [288].

Papers have appeared in which organoarsenic compounds have found biological use, either in antigen-antibody studies [289-294], as feed supplements for poultry or domestic animals [295-298], or as herbicides [299].

## REFERENCES

1 K. Moedritzer, in E. I. Becker and M. Tsutsui, eds., *Organometallic Reactions*, Vol. 2, Wiley-Interscience, New York, 1971, pp. 1-115.

2 N. N. Greenwood, ed., *Spectroscopic Properties of Inorganic and Organometallic Compounds*, Vol. 4, The Chemical Society, London, 1971.

3 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970, p. 57, 484-6.

4 M. Lesbre, P. Mazerolles, and J. Satgé, *The Organic Compounds of Germanium*, Wiley-Interscience, New York, 1971, pp. 488, 669-672.

5 D. D. Davis and C. E. Gray, *Organometallic Chem. Rev., Sect. A,* 6 (1970) 283.

6 R. Colton, *Coord. Chem. Rev.,* 6 (1971) 269.

7 W. R. Cullen and W. R. Leeder, *Can. J. Chem.,* 48 (1970) 3757.

8 B. C. McBride and R. S. Wolfe, *Biochemistry,* 10 (1971) 4312.

9 T. R. Carlton and C. D. Cook, *Inorg. Chem.,* 10 (1971) 2628.

10 R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.,* 93 (1971) 4158.

11 R. B. King and A. Efraty, *J. Amer. Chem. Soc.,* 93 (1971) 564.

12 J. W. Anderson and J. E. Drake, *Can. J. Chem.,* 49 (1971) 2524.

13 D. I. Hall and R. S. Nyholm, *J. Chem. Soc., A,* (1971) 1491.

14 G. Kh. Kamai, R. D. Gigauri, B. D. Chernokal skii, and M. M. Ugulava, *Zh. Obshch. Khim.,* 41 (1971) 1506.

15 R. D. Feltham and H. G. Metzger, *J. Organometal. Chem.,* 33 (1971) 347.

16 H.-S. Kuo and W. L. Jolly, *J. Organometal. Chem.,* 30 (1971) 361.

17 S. S. Sandhu and H. Singh, *J. Inorg. Nucl. Chem.,* 33 (1971) 97.

18 J. W. Dawson and L. M. Venanzi, *J. Chem. Soc., A,* (1971) 2897.

19 E. H. Braye, I. Caplier, and R. Saussez, *Tetrahedron,* 27 (1971) 5523.

20 H. G. Ang and K. F. Ho, *J. Organometal. Chem.,* 27 (1971) 349.

21 J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, *J. Organometal. Chem.,* 27 (1971) 241.

22 Z. Raciszewski and E. H. Braye, *Photochem. Photobiol.,* 12 (1970) 429.

23 J. C. Tou and C.-S. Wang, *Org. Mass Spectrom.,* 4 (1971) 503.

24 R. A. Earley and M. J. Gallagher, *Org. Mass. Spectrom.,* 3 (1970) 1287.

25 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., B,* (1971) 1823.

26 D. Cunningham, M. J. Frazer, and J. D. Donaldson, *J. Chem. Soc., A,* (1971) 2049.

27 T. V. Zykova, G. Kh. Kamai, B. D. Chernokal'skii, R. A. Salakhutdinov, and B. E. Abalonin, *Zh. Obshch. Khim.,* 41 (1971) 1508.

28 C. H. Yoder, R. H. Tuck, and R. E. Hess, *J. Amer. Chem. Soc.,* 91 (1969) 539.

29 R. E. Hess, C. K. Haas, B. A. Kaduk, C. D. Schaeffer, Jr., and C. H. Yoder, *Inorg. Chim. Acta,* 5 (1971) 161.

30 R. R. Shagidullin and A. V. Chernova, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1971) 183.

31 F. T. Delbeke, R. F. de Ketelaere, and G. P. van der Kelen, *J. Organometal. Chem.,* 28 (1971) 225.

32 R. F. de Ketelaere, F. T. Delbeke, and G. P. van der Kelen, *J. Organometal. Chem.,* 28 (1971) 217.

33 G. M. Bogolyubov, N. N. Grishin, and A. A. Petrov, *Zh. Obshch. Khim.,* 41 (1971) 1710.

34 A. J. Carty, N. K. Hota, T. W. Ng, H. A. Patel, and T. J. O'Connor, *Can. J. Chem.,* 49 (1971) 2706.

35 W. R. Cullen, D. C. Frost, and W. R. Leeder, *J. Fluorine Chem.,* 1 (1971/72) 227.

36 W. M. A. Smit and G. Dijkstra, *J. Mol. Struct.,* 8 (1971) 263.

37 L. M. Épshtein, Z. S. Novikova, L. D. Ashkinadze, S. O. Rabicheva, and L. A. Kazitsyna, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1970) 2379.

38 A. L. Balch, *Inorg. Chem.,* 10 (1971) 276.

39 A. J. Cheney and B. L. Shaw, *J. Chem. Soc., A,* (1971) 3549.

40 J. J. Bishop and A. Davison, *Inorg. Chem.,* 10 (1971) 832.

41 B. Chiswell and K. A. Verrall, *J. Prakt. Chem.,* 312 (1971) 751.

42 B. R. Cook, C. A. McAuliffe, and D. W. Meek, *Inorg. Chem.,* 10 (1971) 2676.

43 J. W. Dawson, B. C. Lane, R. J. Mynott, and L. M. Venanzi, *Inorg. Chim. Acta,* 5 (1971) 25.

44 J. Brobe and F. Kober, *J. Organometal. Chem.,* 29 (1971) 295.

45 W. Ehrl and H. Vahrenkamp, *Chem. Ber.,* 104 (1971) 3261.

46 J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organometal. Chem.,* 29 (1971) 105.

47 F. T. Delbeke, E. G. Claeys, and G. P. van der Kelen, *J. Organometal. Chem.,* 28 (1971) 391.

48 G. B. Robertson, P. O. Whimp, R. Colton, and C. J. Rix, *J. Chem. Soc., D,* (1971) 573.

49 H. G. Metzger and R. D. Feltham, *Inorg. Chem.,* 10 (1971) 951.

50 E. O. Fischer, W. Bathelt and J. Müller, *Chem. Ber.,* 104 (1971) 986.

51 R. Colton and C. J. Rix, *Aust. J. Chem.,* 24 (1971) 2461.

52 J. J. Bishop and A. Davison, *Inorg. Chem.,* 10 (1971) 826.

53 P. C. Ellgen, *Inorg. Chem.,* 10 (1971) 232.

54 M. A. Bennett and J. D. Wild, *J. Chem. Soc., A,* (1971) 545.

55 N. Maki and K. Ohshima, *Bull Chem. Soc. Jap.,* 43 (1970) 3970.

56 N. K. Hota, H. A. Patel, A. J. Carty, M. Mathew, and G. J. Palenik, *J. Organometal. Chem.,* 32 (1971) C55.

57 B. Chiswell, R. A. Plowman, and K. Verrall, *Inorg. Chim. Acta,* 5 (1971) 579.

58 A. Peloso and L. Volponi, *Gazz. Chim. Ital.,* 100 (1970) 825.

59 J. F. White and M. F. Farona, *Inorg. Chem.,* 10 (1971) 1080.

60 W. Harrison and J. Trotter, *J. Chem. Soc., A,* (1971) 1607.

61 S. S. Sandhu and S. S. Parmar, *J. Chem. Soc., A,* (1971) 111.

62 J. Ellermann and W. Uller, *Chem. Ber.,* 103 (1970) 3932.

63 R. A. Zelonka and M. C. Baird, *J. Chem. Soc., D,* (1971) 780.

64 W. T. Reichle, *Inorg. Chim. Acta,* 5 (1971) 325.

65 D. Negoiu, M. Negoiu, and F. Ilinca, *An. Univ. Bucaresti, Chim.,* 18 (1969) 139; *Chem. Abstr.,* 75 (1971) 94165f.

66 F. H. Jardine, A. G. Vohra, and F. J. Young, *J. Inorg. Nucl. Chem.,* 33 (1971) 2941.

67 R. Graziani, G. Bombieri, and E. Forsellini, *J. Chem. Soc., A,* (1971) 2331.

68 S. S. Sandhu and H. Singh, *J. Inorg. Nucl. Chem.,* 33 (1971) 1457.

69 F. H. Jardine and F. J. Young, *J. Chem. Soc., A,* (1971) 2444.

70 G. C. Stocco and R. S. Tobias, *J. Amer. Chem. Soc.,* 93 (1971) 5057.

71 F. Stocco, G. C. Stocco, W. M. Scovell, and R. S. Tobias, *Inorg. Chem.,* 10 (1971) 2639.

72 M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 93 (1971) 4591.

73 S. S. Sandhu and R. S. Sandhu, *Indian J. Chem.*, 9 (1971) 482.

74 G. K. N. Reddy and E. G. Leelamani, *Proc. Chem. Symp., 2nd,* 1 (1970) 247; *Chem. Abstr.*, 76 (1972) 146924v.

75 H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *J. Chem. Soc., D,* (1970) 1694.

76 G. Wilkinson, C. K. Brown, W. Mowat, and G. Yagupsky, *J. Chem. Soc., A,* (1971) 850.

77 G. L. McClure and W. H. Baddley, *J. Organometal. Chem.*, 27 (1971) 155.

78 R. G. Cunningham, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc., A,* (1971) 227.

79 L. Vaska and J. Peone, Jr., *Suom. Kemistilehti, B,* 44 (1971) 317.

80 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., A,* (1971) 1254.

81 B. L. Shaw and R. M. Slade, *J. Chem. Soc., A,* (1971) 1184.

82 L. M. Haines and E. Singleton, *J. Organometal. Chem.*, 30 (1971) C81.

83 P. R. Brookes, C. Masters, and B. L. Shaw, *J. Chem. Soc., A,* (1971) 3756.

84 W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 10 (1971) 843.

85 J. Miller and A. L. Balch, *Inorg. Chem.*, 10 (1971) 1410.

86 J. A. de Beer, R. J. Haines, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc., A,* (1971) 3271.

87 F. W. B. Einstein, A.-M. Pilotti, and R. Restivo, *Inorg. Chem.*, 10 (1971) 1947.

88 J.-J. Legendre, C. Girard, and M. Huber, *Bull. Soc. Chim. Fr.*, (1971) 1998.

89 J. P. Crow, W. R. Cullen, F. L. Hou, L. Y. Y. Chan, and F. W. B. Einstein, *J. Chem. Soc., D,* (1971) 1229.

90 S. S. Sandhu and A. K. Mehta, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 891.

91 R. H. Reimann and E. Singleton, *J. Organometal. Chem.,* 32 (1971) C44.

92 A. J. Canty and B. M. Gatehouse, *J. Chem. Soc., D,* (1971) 443.

93 T. A. James and J. A. McCleverty, *J. Chem. Soc., A,* (1971) 1596.

94 M. G. B. Drew, A. W. Johans, A. P. Wolters, and I. B. Tomkins, *J. Chem. Soc., D,* (1971) 819.

95 I. W. Nowell and J. Trotter, *J. Chem. Soc., A,* (1971) 2922.

96 M. W. Anker, R. Colton, and C. J. Rix, *Aust. J. Chem.,* 24 (1971) 1157.

97 P. T. Roberts and J. Trotter, *J. Chem. Soc., A,* (1971) 1501.

98 W. R. Cullen, I. W. Nowell, P. J. Roberts, J. Trotter, and J. E. H. Ward, *J. Chem. Soc., D,* (1971) 560.

99 D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.,* 93 (1971) 2807.

100 M. W. Anker and R. Colton, *Aust. J. Chem., A,* (1971) 2223.

101 M. A. Bennett and J. D. Wild, *J. Chem. Soc., A,* (1971) 536.

102 J. Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc., A,* (1971) 453.

103 N. Almasi, St. Farkas, and E. Cimpianu, *Stud. Univ. Babes-Bolyai, Ser. Chem* 16 (1971) 101; *Chem. Abstr.,* 76 (1972) 13436r.

104 B. Baracco, M. T. Halfpenny, and C. A. McAuliffe, *J. Chem. Soc., D,* (1971) 1502.

105 B. R. Higginson, C. A. McAuliffe, and L. M. Venanzi, *Inorg. Chim. Acta,* 5 (1971) 37.

106 M. Di Vaira, *J. Chem. Soc., A,* (1971) 148.

107 J. R. Ferraro, *Inorg. Nucl. Chem., Lett.,* 6 (1970) 823.

108 D. Negoiu and I. Serban-Teodosescu, *An. Univ. Bucaresti, Chim.,* 19 (1970) 101; *Chem. Abstr.,* 75 (1971) 94162c.

109 J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc., A,* (1971) 1169.

110 R. Ros and E. Tondello, *J. Inorg. Nucl. Chem.,* 33 (1971) 245.

111 M. Nonoyama and K. Yamasaki, *Nippon Kagaku Zasshi,* 91 (1971) 1058; *Chem. Abstr.,* 74 (1971) 68397t.

112 D. Negoiu and V. Serban, *Rev. Roum. Chim.*, 16 (1971) 1347.

113 D. Negoiu and V. Serban, *An. Univ. Bucaresti, Chim.*, 19 (1970) 45; *Chem. Abstr.*, 76 (1972) 9933h.

114 T. D. B. Morgan and M. L. Tobe, *Inorg. Chim. Acta*, 5 (1971) 563.

115 P. L. Goggin, R. J. Knight, L. Sindellari, and L. M. Venanzi, *Inorg. Chim. Acta*, 5 (1971) 62.

116 J. N. Crosby and R. D. W. Kemmitt, *J. Organometal. Chem.*, 26 (1971) 277.

117 T. Boschi, P. Uguagliati, and B. Crociani, *J. Organometal. Chem.*, 30 (1971) 283.

118 P. S. Braterman, V. A. Wilson, and K. K. Joshi, *J. Organometal. Chem.*, 31 (1971) 123.

119 J. P. Beale, L. F. Lindoy, S. E. Livingstone, and N. C. Stephenson, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 851.

120 J. L. Burmeister and F. Basolo, *Inorg. Syn.*, 12 (1970) 218.

121 J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *J. Chem. Soc., D*, (1970) 67

122 H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc., A*, (1971) 3472.

122a S. S. Sandhu and H. Singh, *Indian J. Chem.*, 9 (1971) 157.

123 H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 10 (1971) 416.

124 H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 10 (1971) 18.

125 M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *J. Organometal. Chem.*, 26 (1971) 293.

126 M. H. Chisholm, H. C. Clark, and D. H. Hunter, *J. Chem. Soc., D*, (1971) 809.

127 D. M. Blake and R. Mersecchi, *J. Chem. Soc., D*, (1971) 1045.

128 P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Amer. Chem. Soc.*, 93 (1971) 5424.

129 H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 10 (1971) 2699.

130 D. Negoiu and V. Serban, *An. Univ. Bucaresti, Chim.*, 18 (1969) 113; *Chem. Abstr.*, 74 (1971) 106695y.

131 A. Peloso, *Gazz. Chim. Ital.*, 100 (1970) 851.

132 A. J. Cheney, B. E. Mann, and B. L. Shaw, *J. Chem. Soc.*, *D*, (1971) 431.

133 J. P. Beale and N. C. Stephenson, *Acta Crystallogr.*, *Sect. B*, 27 (1971) 73.

134 R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, 10 (1971) 1820.

135 G. W. Watt and J. E. Cuddeback, *Inorg. Chem.*, 10 (1971) 947.

136 J. J. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, 10 (1971) 2032.

137 J. M. C. Alison, T. A. Stephenson, and R. O. Gould, *J. Chem. Soc.*, *A*, (1971) 3690.

138 M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Chem. Soc.*, *D*, (1971) 1627.

139 A. J. Cheney and B. L. Shaw, *J. Chem. Soc.*, *A*, (1971) 3545.

140 W. Himmele, W. Aquila, and F. J. Mueller (Badische Anilin und Soda-Fabrik A.-G.), Ger. Offen. 1,957,300; *Chem. Abstr.*, 75 (1971) 36336b.

141 B. L. Booth, M. J. Else, R. Fields, and R. N. Haszeldine, *J. Organometal. Chem.*, 27 (1971) 119.

142 D. F. Steele and T. Stephenson, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 877.

143 Yu. N. Kukushkin, L. I. Danilina, and M. M. Syngh, *Zh. Neorg. Khim.*, 16 (1971) 2718.

144 J. T. Mague, *J. Amer. Chem. Soc.*, 93 (1971) 3550.

145 L. M. Haines, *Inorg. Chem.*, 10 (1971) 1685.

146 F. Glockling and G. C. Hill, *J. Chem. Soc.*, *A*, (1971) 2137.

147 D. P. Rice and J. A. Osborn, *J. Organometal. Chem.*, 30 (1971) C84.

148 P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, 93 (1971) 84.

149 B. E. Prater, *J. Organometal. Chem.*, 27 (1971) C17.

150 B. E. Prater, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 1071.

151 R. E. Townsend and K. J. Coskran, *Inorg. Chem.*, 10 (1971) 1661.

152 P. J. Roberts and J. Trotter, *J. Chem. Soc.*, *A*, (1971) 1479.

153 S. Vasudevan and K. N. Kuchela, *Curr. Sci.*, 40 (1971) 265.

154 M. T. Halfpenny and L. M. Venanzi, *Inorg. Chim. Acta*, 5 (1971) 91.

155 T. J. Marks, J. S. Kristoff, A. Alich, and D. F. Shriver, *J. Organometal. Chem.*, 33 (1971) C35.

156 T. L. Blundell and H. M. Powell, *J. Chem. Soc., A*, (1971) 1685.

157 S. S. Sandhu and H. Singh, *Indian J. Chem.*, 9 (1971) 267.

158 A. Davison and J. E. Ellis, *J. Organometal. Chem.*, 31 (1971) 239.

159 Yu. F. Gatilov, L. B. Ionov, and F. D. Yambushev, *Zh. Obshch. Khim.*, 41 (1971) 570.

160 Yu. F. Gatilov, L. B. Ionov, and F. D. Yambushev, *Zh. Obshch. Khim.*, 40 (1970) 2250.

161 H. Kessler, *Naturwissenschaften*, 58 (1971) 46.

162 J.-P. Fayet and P. Mauret, *J. Chim. Phys. Physiochim. Biol.*, 68 (1971) 156.

163 K. Sommer, W. Lauer, and M. Becke-Goehring, *Z. Anorg. Allg. Chem.*, 379 (1970) 48.

164 J. Koketsu and Y. Ishii, *J. Chem. Soc., C*, (1971) 2.

165 Yu. L. Kopaevich, G. G. Belen'kii, L. S. German, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 1124.

166 B. Tittle (Imperial Chemical Industries Ltd.), Brit. Pat. 1,223,126; *Chem. Abstr.*, 75 (1971) 20624h.

167 J. R. Durig, C. F. Jumper, and J. N. Willis, Jr., *Appl. Spectrosc.*, 25 (1971) 218.

168 K. Sommer, *Z. Anorg. Allg. Chem.*, 383 (1971) 136.

169 C.-S. Wang and T. W. McGee (Dow Chemical Co.), U.S. Pat. 3,544,610; *Chem. Abstr.*, 74 (1971) 64308s.

170 C.-S. Wang and T. W. McGee (Dow Chemical Co.), U.S. Pat. 3,547,967; *Chem. Abstr.*, 74 (1971) 88135j.

171 T. Zsolnai, *Zentralbl. Bakteriol., Parasitenk., Infektionskr. Hyg., Abt. I: Orig.*, 214 (1970) 507; *Chem. Abstr.*, 74 (1971) 61962q.

172 B. E. Abalonin, B. D. Chernokal'skii, R. R. Shagidullin, S. V. Izosimova, T. V. Zykova, and G. Kamai, *Zh. Obshch. Khim.*, 40 (1970) 1812.

173 J. Müller, *Z. Anorg. Allg. Chem.*, 381 (1971) 103.

174 J. W. Anderson and J. E. Drake, *J. Chem. Soc., D*, (1971) 1372.

175 R. H. Anderson and R. H. Cragg, *J. Chem. Soc., D*, (1971) 1414.

176 H. Vahrenkamp, *J. Organometal. Chem.*, 28 (1971) 167.

177 B. A. Arbuzov, L. K. Yuldasheva, N. A. Chadaeva, R. P. Arshinova, I. V. Anonimova, and G. Kh. Kamai, *Dokl. Akad. Nauk SSSR*, 200 (1971) 97.

178 L. I. Zakharkin and V. I. Kyskin, *Izv. Acad. Nauk SSSR, Ser. Khim.*, (1971) 2053.

179 N. A. Chadaeva, G. Kh. Kamai, and K. A. Mamakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 1726.

180 V. Krieg and J. Weidlein, *Angew. Chem., Int. Ed. Engl.*, 10 (1971) 516.

181 R. Demuth, J. Grobe, and L. Steiner, *Z. Naturforsch., B*, 26 (1971) 731.

182 P. S. Elmes, P. Leverett, and B. O. West, *J. Chem. Soc., D*, (1971) 747.

182a P. S. Elmes and B. O. West, *J. Organometal. Chem.*, 32 (1971) 365.

183 N. Camerman and J. Trotter, *J. Chem. Soc.*, (1964) 219.

184 R. A. Zingaro, K. J. Irgolic, D. H. O'Brien, and L. J. Edmonson, Jr., *J. Amer. Chem. Soc.*, 93 (1971) 5677.

185 A. J. Ashe, III, *J. Amer. Chem. Soc.*, 93 (1971) 3293.

186 N. Mandel and J. Donohue, *Acta Crystallogr., Sect. B.*, 27 (1971) 476.

187 G. Kh. Kamai, B. E. Abalonin, B. D. Chernokal'skii, S. V. Izosimova, and R. R. Shagidulin, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 14 (1971) 724; *Chem. Abstr.*, 75 (1971) 76964m.

188 A. K. Panigrahi, P. L. Nayak, and M. K. Rout, *J. Inst. Chem., Calcutta*, 42 (1970) 226; *Chem. Abstr.*, 74 (1971) 141997v.

189 K. J. Irgolic, L. R. Kallenbach, and R. A. Zingaro, *J. Inorg. Nucl. Chem.*, 33 (1971) 3177.

190 M. Basato and A. Peloso, *Gazz. Chim. Ital.*, 101 (1971) 281.

191 A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., D*, (1971) 1068.

192 A. Watson, W. F. Smyth, G. Svehla, and K. Vadasdi, *Fresenius' Z. Anal. Chem.*, 253 (1971) 106.

193 S. S. Sandhu and G. S. Aulakh, *Indian J. Chem.*, 9 (1971) 721.

194 S. S. Sandhu and G. K. Sandhu, *Indian J. Chem.*, 9 (1971) 885.

195 L. D. Freedman, G. O. Doak, and B. R. Ezzell, *Microchem. J.*, 16 (1971) 311.

196 M. R. Smith, R. A. Zingaro, and E. A. Meyers, *Thermochim. Acta*, 1 (1970) 555.

197 M. R. Smith, R. A. Zingaro, and E. A. Meyers, *J. Organometal. Chem.*, 27 (1971) 341.

198 B. Kamieński and E. Krauss, *Bull. Acad. Pol. Sci., Ser. Sci: Chim.*, 19 (1971) 347.

199 N. S. Frumina, M. L. Nikurashina, and E. G. Tregub, USSR Pat. 295,769; *Chem. Abstr.*, 75 (1971) 63979v.

200 J. W. Nemec, H. R. Raterink, and S. W. Wise (Rohm and Haas Co.), U.S. Pat. 3,586,708; *Chem. Abstr.*, 75 (1971) 63981q.

201 M. Kranz, W. Duczmal, and K. Langowska, *Chem. Anal. (Warsaw)*, 16 (1971) 399; *Chem. Abstr.*, 75 (1971) 58263c.

202 N. N. Basargin, M. K. Akhmedli, and Sh. U. Islamov, *Zavod. Lab.*, 37 (1971) 269.

203 Z. Holzbecher and K. Volka, *Collect. Czech. Chem. Comm.*, 35 (1970) 2925.

204 A. T. Pilipenko and L. L. Shevchenko, *Zh. Neorg. Khim.*, 16 (1971) 2124.

205 K. Kina and K. Tôei, *Bull. Chem. Soc. Jap.*, 44 (1971) 2416.

206 B. D. Chernokal'skii, Sh. G. Enikeev, R. B. Bairamov, A. K. Kaviev, and G. Kamai, *Zh. Obshch. Khim.*, 40 (1970) 2648.

207 G. M. Usacheva and G. Kh. Kamai, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1968) 1878.

208 G. M. Usacheva and G. Kh. Kamai, *Zh. Obshch. Khim.*, 40 (1970) 1306.

209 G. M. Usacheva and G. Kh. Kamai, *Izv. Akad. Nauk SSSR., Ser. Khim.*, (1971) 168.

210 V. I. Gavrilov, B. D. Chernokal'skii, and G. Kh. Kamai, *Zh. Obshch. Khim.*, 41 (1971) 560.

211 V. I. Gavrilov, L. A. Batina, B. D. Chernokal'skii, and G. Kh. Kamai, *Zh. Obshch. Khim.*, 41 (1971) 564.

212 B. D. Chernokal'skii, B. E. Abalonin, R. R. Shagidullin. S. V. Izosimova, and G. Kamai, *Zh. Obshch. Khim.*, 40 (1970) 2645.

213 G. Kh. Kamai, B. D. Chernokal'skii, and L. I. Moisak, *Zh. Obshch. Khim.*, 41 (1971) 1287.

214 D. A. Davenport, F. F. Farris, and W. R. Robinson, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 613.

215 F. F. Farris and W. R. Robinson, *J. Organometal. Chem.*, 31 (1971) 375.

216 Yu. M. Kargin, N. I. Semakhina, B. D. Chernokal'skii, A. S. Gel'fond and G. Kh. Kamai, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1970) 2488.

217 F. Choplin and G. Kaufmann, *Spectrochim. Acta, Part A*, 26 (1970) 2113.

218 R. Bravo, M. Durand, J.-P. Laurent, and F. Gallais, *C. R. Acad. Sci., Ser. C.*, 273 (1971) 37.

219 S. Milićev and D. Hadži, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 745.

220 H. R. Leene, G. DeVries, and U. A. Th. Briahman, *J. Chromatogr.*, 57 (1971) 173.

221 L. Horner, H. Hinrichs, and H. Ertel, *Werkst. Korros.*, 22 (1971) 930; *Chem. Abstr.*, 76 (1972) 48788j.

222 N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski, and M. M. Labes, *J. Inorg. Nucl. Chem.*, 33 (1971) 2691.

223 G. B. Deacon and J. C. Parrott, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 329.

224 S. A. Cotton and J. F. Gibson, *J. Chem. Soc., A*, (1971) 859.

225 F. Mani, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 447.

226 B. Zarli, R. Graziani, E. Forsellini, U. Croatto, and G. Bombieri, *J. Chem. Soc., D*, (1971) 1501.

227 O. Gürtler, H. Holzapfel, and Chu-Xuan-Anh, *Z. Chem.*, 11 (1971) 389.

228 L. Zimmer and K. H. Lieser, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 1163.

229 C. G. Moreland, R. J. Beam, C. W. Wooten, and S. M. Horner, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 243.

230 M. H. O'Brien, G. O. Doak, and G. G. Long, *Inorg. Chim. Acta,* 1 (1967) 34.

231 M. B. Hursthouse and I. A. Steer, *J. Organometal. Chem.*, 27 (1971) C11.

232 Yu. F. Gatilov, G. Kh. Kamai, and R. R. Shagidullin, *Zh. Obshch. Khim.*, 36 (1966) 1670.

233 Yu. F. Gatilov and V. P. Kovyrzina, *Zh. Obshch. Khim.*, 41 (1971) 567.

234 Yu. F. Gatilov, M. G. Kralichkina, and V. P. Kovyrzina, *Zh. Obshch. Khim.*, 41 (1971) 1291.

235 E. W. Ainscough, A. M. Brodie, and A. R. Furness, *J. Chem. Soc., D,* (1971) 1357.

236 B. D. Chernokal'skii, I. B. Levenshtein, and G. Kh. Kamai, *Zh. Obshch. Khim.*, 41 (1971) 557.

237 G. Kh. Kamai, B. D. Chernokal'skii, and I. B. Levenshtein, *Zh. Obshch. Khim.*, 41 (1971) 2015.

238 P. Frøyen, *Acta Chem. Scand.*, 25 (1971) 983.

239 P. Frøyen, *Acta Chem. Scand.*, 25 (1971) 2781.

240 M. Espeillac and D. Decroocq, *Bull. Soc. Chim. Fr.* (1971) 2418.

241 V. V. Gavrilenko, Yu. N. Karaksin, and L. I. Zakharkin, *Zh. Obshch. Khim.*, 41 (1971) 1511.

242 P. Schipper and H. M. Buck, *Phosphorus,* 1 (1971) 93.

243 D. Cashman and F. J. Lalor, *J. Organometal. Chem.*, 32 (1971) 351.

244 T. Austad, J. Songstad, and L. J. Stangeland, *Acta Chem. Scand.*, 25 (1971) 2327.

245 A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 10 (1971) 2720.

246 T. V. Zykova, G. Kh. Kamai, B. D. Chernokal'skii, R. A. Salakhutdinov, and B. E. Abalonin, *Zh. Obshch. Khim.*, 41 (1971) 1044.

247 J. Jolicoeur, N. D. The, and A. Cabana, *Can. J. Chem.*, 49 (1971) 2008.

248 J. F. Coetzee and W. R. Sharpe, *J. Phy. Chem.*, 75 (1971) 3141.

249 D. W. Larsen, *J. Phy. Chem.*, 75 (1971) 3880.

250 J. B. Orenberg, M. D. Morris, and T. V. Long, II, *Inorg. Chem.*, 10 (1971) 933.

251 E. J. Baran, *Z. Anorg. Allg. Chem.*, 382 (1971) 80.

252 L. K. Walford, R. J. Blattner, S. Feldman, and R. L. Bain, *Can. J. Chem.*, 48 (1970) 2637.

253 F. J. Millero, *J. Phys. Chem.*, 75 (1971) 280.

254 F. J. Millero, *J. Chem. Eng. Data*, 16 (1971) 229.

255 K. Ohkubo, *Tetrahedron Lett.*, (1971) 2571.

256 Y. Iida, *Bull. Chem. Soc. Jap.*, 43 (1970) 3685.

257 V. M. Tsentovskii, V. P. Barabanov, G. Kh. Kamai, B. D. Chernokal'skii, B. D. Abalonin, and T. A. Busygina, *Zh. Obshch. Khim.*, 41 (1971) 1047.

258 A. T. McPhail, G. M. Semeniuk, and D. B. Chesnut, *J. Chem. Soc., A*, (1971) 2174.

259 J. R. Brand and M. L. Smith, *Anal. Chem.*, 43 (1971) 1105.

260 R. Ismail (Dynamit Nobel A.-G.) Fr. Pat. 1,592,401; *Chem. Abstr.*, 74 (1971) 42880v.

261 M. Ogata, M. Sato, Y. Watanabe, and H. Suzuki (Hitachi, Ltd.), Ger. Offen. 2,025,469; *Chem. Abstr.*, 74 (1971) 43048s.

262 W. R. Robinson and D. P. Schussler, *J. Organometal. Chem.*, 30 (1971) C5.

263 M.-A. Buhannic and J. E. Guerchais, *Bull. Soc. Chim. Fr.*, (1971) 55.

264 L. I. Zakharkin, V. V. Gavrilenko, and Yu. N. Karaksin, *Syn. Inorg. Metal-Org. Chem.*, 1 (1971) 37.

265 K. K. Ganguli, G. O. Carlisle, H. J. Hu, L. J. Theriot, and I. Bernal, *J. Inorg. Nucl. Chem.*, 33 (1971) 3579.

266 N. Brničević and C. Djordjević, *J. Less-Common Metals*, 23 (1971) 61.

267 T. Austad, J. Songstad, and K. Åse, *Acta Chem. Scand.*, 25 (1971) 1136.

268 G. N. Bilimovich and N. N. Churkina, *J. Radioanal. Chem.*, 8 (1971) 53.

269 T. Austad, J. Songstad, and K. Åse, *Acta Chem. Scand*, 25 (1971) 331.

270 M. Široki and C. Djordjevic, *Anal. Chim. Acta,* 57 (1971) 301.

271 A. T. Casey, R. J. H. Clark, R. S. Nyholm, and D. E. Scaife, *Inorg. Syn.,* 13 (1971) 165.

272 D. Lloyd and M. I. C. Singer, *J. Chem. Soc., C,* (1971) 2941.

273 A. J. Dale and P. Frøyen, *Acta Chem. Scand.,* 24 (1970) 3772.

274 P. Frøyen, *Acta Chem. Scand.,* 25 (1971) 2541.

275 G. Ferguson, D. F. Rendle, D. Lloyd, and M. I. C. Singer, *J. Chem. Soc., D,* (1971) 1647.

276 A. V. Fokin, Yu. N. Studnev, L. D. Kuznetsova, and A. F. Kolomiets, *Zh. Obshch. Khim.,* 41 (1971) 486.

277 N. A. Nesmeyanov, E. V. Binshtok, and O. A. Reutov, *Dokl. Akad. Nauk SSSR,* 198 (1971) 1102.

278 E. E. Ernstbrunner and D. Lloyd, *Chem. Ind.* (London), (1971) 1332.

279 A. J. Dale and P. Frøyen, *Acta Chem. Scand.,* 25 (1971) 1452.

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

281 N. A. Nesmeyanov and V. V. Mikul'shina, *Zh. Org. Khim.,* 7 (1971) 696.

282 R. Trippett and M. A. Walker, *J. Chem. Soc., C,* (1971) 1114.

283 P. Bravo, G. Gaudiano, P. P. Ponti, and M. G. Zubiani, *Tetrahedron Lett.* (1970) 4535.

284 D. Hellwinkel and B. Knake, *Chem. Ber.,* 104 (1971) 1761.

285 C.-S. Wang and T. W. McGee (Dow Chemical Co.) U.S. Pat. 3,542,827; *Chem. Abstr.,* 75 (1971) 6102e.

286 O. J. Scherer and W. Gick, *Chem. Ber.,* 104 (1971) 1490.

287 S. S. Sandhu, S. S. Pahil, and K. D. Sharma, *Anal. Chim. Acta,* 56 (1971) 154.

288 C. Cosovic and V. Karas-Gasparec, *Farm. Glas.,* 26 (1970) 255; *Chem. Abstr.,* 74 (1971) 49421e.

289 S. Leskowitz, H. B. Richerson, and H. J. Schwartz, *Immunochemistry,* 7 (1970) 949.

290 W. D. Behnke and B. L. Vallee, *Biochem. Biophys. Res. Commun.*, 43 (1971) 760.

291 J. D. Clough, L. H. Mims, and W. Strober, *J. Immunol.*, 106 (1971) 1624.

292 O. D. Gulati and D. G. Patel, *Brit. J. Pharmacol.*, 42 (1971) 66.

293 C.-Y. Wu and B. Cinader, *J. Exp. Med.*, 134 (1971) 693.

294 L. T. Rosenberg, A. A. Amkraut, R. B. Corp, and S. Raffel, *J. Immunol.*, 107 (1971) 1175.

295 R. S. Barber, R. Braude, and K. G. Mitchell, *Brit. J. Nutr.*, 25 (1971) 381.

296 R. E. Weston, B. B. Wheals, and M. J. Kensett, *Analyst* (London), 96 (1971) 601.

297 T. E. Bowen, T. W. Sullivan, and O. D. Grace, *Poultry Sci.*, 50 (1971) 861.

298 H. W. Hulan and N. Nikolaiczuk, *Can. J. Anim. Sci.*, 51 (1971) 169.

299 P. E. Keeley and R. J. Thullen, *Weed. Sci.*, 19 (1971) 297.