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Compounds of dicoordinate arsenic: chemical properties

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ABSTRACT. The present review presents the known types of compounds of dicoordinate arsenic ($\lambda^3\sigma^2$As) with the exception of compounds with a formally charged dicoordinate arsenic atom. Data on the reactivity of the $\lambda^3\sigma^2$As systems are surveyed and described systematically. It is shown that the most characteristic and the most thoroughly investigated property is addition to a multiple or diene bond involving an arsenic atom. Certain cyclic $\lambda^3\sigma^2$As derivatives are known to exhibit the properties of aromatic compounds. The ability of derivatives of dicoordinate arsenic to behave as ligands in complex formation reactions involving the As atom, the As–X bonds (X = C, As, P), or the entire π-bond system is reported.

The bibliography includes 109 references.

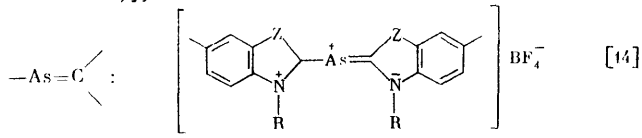
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I. Introduction

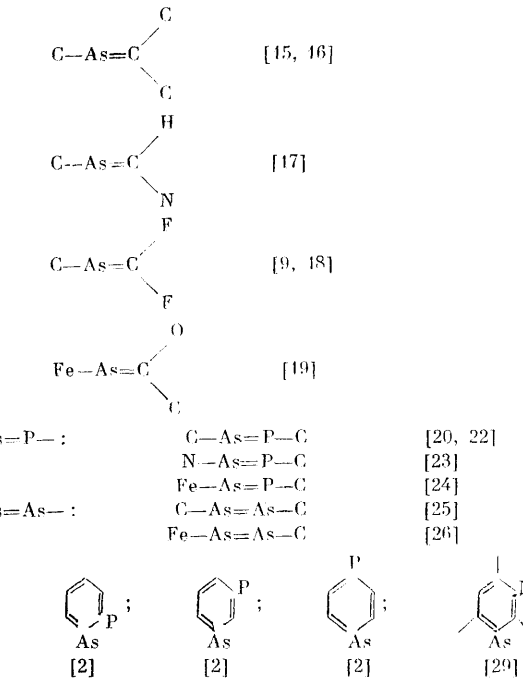
As a consequence of the unusual coordination and the unusual reactivity, compounds of phosphorus and arsenic atoms involved in a low coordination have continually attracted the attention of chemists. Studies in the field of monocoordinate and dicoordinate phosphorus have appreciably overtaken the development of the chemistry of analogous organoarsenic derivatives. A whole series of review articles have been devoted to compounds of dicoordinate phosphorus ($\lambda^3\sigma^2$P).[1–12] There are virtually no reviews on $\lambda^3\sigma^2$As systems. As regards compounds of monocoordinate arsenic, the existence of a single representative is known: 2,4,6-t-$Bu_3C_6H_2$–C≡As.[13] This review surveys the results of the authors' own studies and the literature data on the reactivity of $\lambda^3\sigma^2$As compounds.

The known types of $\lambda^3\sigma^2$As derivatives are presented below {the literature references are given for the first representatives of the series [the numerals in square brackets denote references (Ed. of Translation)]}.

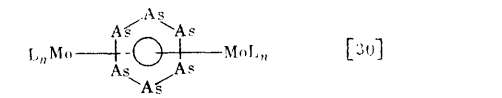


[14]

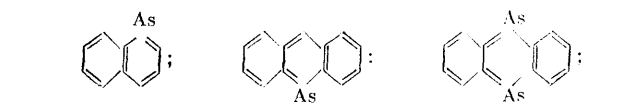
Z = S, CH=CH



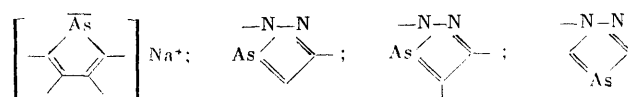
[15, 16] [17] [9, 18] [19] [20, 22] [23] [24] [25] [26] [27, 28] [2] [2] [2] [29]



[30]



[31] [32, 33] [32]* [34] [35] [36] [37]

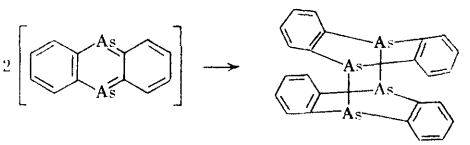


[38] [39] [40] [41]

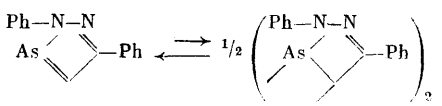
* Detected in the form of primary unstable products.

II. Dimerisation and 1,2-addition

The first data on the chemical properties of derivatives of dicoordinate arsenic concern their instability and tendency to dimerise. Thus, when an attempt was made to synthesise 9,10-diarsaanthracene,[32] its dimer was obtained:

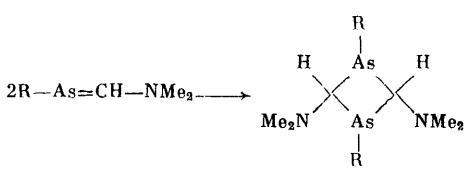


In the synthesis and on prolonged storage of 2,5-diphenyl-1,2,3-diazaarsole, we observed[42] its partial dimerisation. It was noted that there is a mobile equilibrium between the monomer and the dimer, the displacement of which in one direction or another depends on the nature of the solvent. Thus, in ether, benzene, and CH_2Cl_2, diazaarsole dimerises, while in solution in isooctane the dimer associates into the monomer, which was established with the aid of UV spectra:

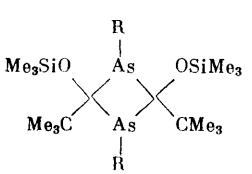


2,5-Diphenyl-1,2,3-diazarsole dimerises faster than it interacts with trichloroacetyl isocyanate or diphenyldiazomethane at room temperature.

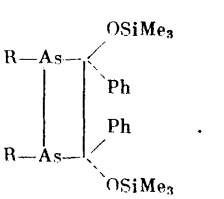
Dimerisation also takes place in the case of acyclic $\lambda^3\sigma^2$As compounds. Thus the ready dimerisation of compounds with the $\lambda^3\sigma^2$As=C bond has been noted:[17]



Two types of dimerisation with formation of 1,2- or 1,3-diarsaethanes have been observed:[43]



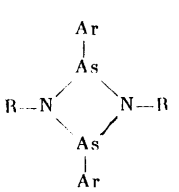
R = Me, Et, $PhCH_2$



R = iso-Pr

In the case of perfluoroheteroalkenes[9] $F_3C-E=CF_2$ (E = P, As), a much greater tendency towards the dimerisation of arsaalkenes than of phosphaalkenes was noted.[9]

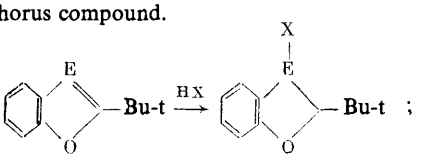
The attempts to obtain derivatives with the $\lambda^3\sigma^2$As=N bond[44,45] led to a negative result. The authors isolated diazadiarsetidines.



The structure of the compound with R = *p*-BrC_6H_4 was demonstrated by X-ray diffraction.

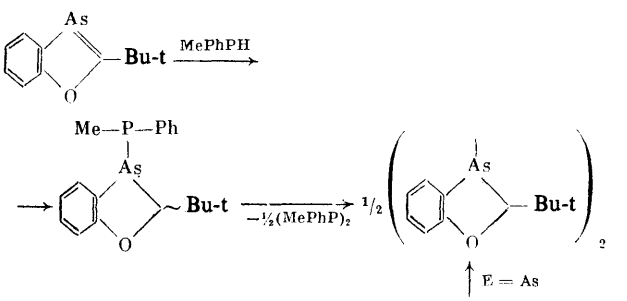
1,3-Benzoxa- and benzaza-arsoles can be classified as unsaturated compounds in terms of their tendency to undergo 1,2-addition reactions.[46]

2-t-Butyl-1,3-benzoxazarsoles and the corresponding phosphole combine with "soft" bases at the E=C bond (E = As, P). The arsenic-containing compound is more reactive than the analogous phosphorus compound.

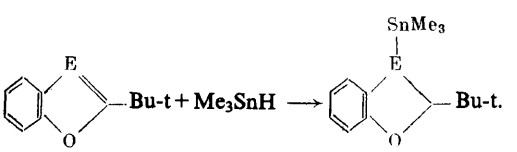


X = I, LL, SPh.

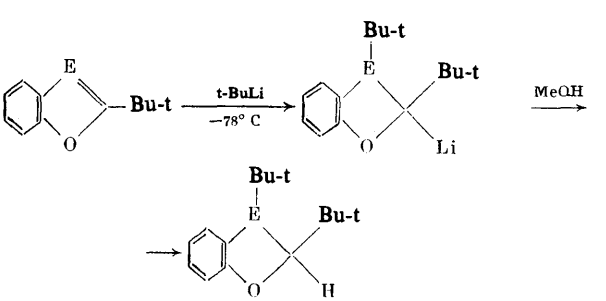
The higher reactivity of the compound with the As=C bond has been observed also in the reactions with methylphenylphosphine and phenylarsine. The reactions proceed in accordance with the following mechanism:



The addition of trimethyltin hydride takes place at the As=C and P=C bonds in 1,3-benzoxaarsole and 1,3-benzoxaphosphole:

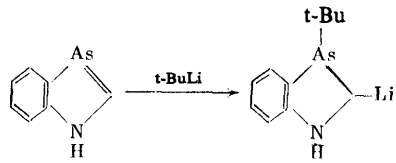


t-Butyllithium also adds to the E=C bond (E = As, P):



In contrast to 1,3-benzoxaarsoles, 1,3-benzazaarsoles show a greater tendency to undergo alkylation or metallation reactions (see Section V) than 1,2-addition reactions with participation of the As=C bond. Thus, among the known 1,3-benzazaarsoles, only the

unsubstituted 1,3-benzazaarsole reacts with t-butyllithium via the 1,2-addition mechanism:[47]



In the case of substituted 1,3-benzazaarsoles or other organolithium reagents, metallation in the 1- or 2-position in the ring takes place.

The above difference in the chemical behaviour of 1,3-benzazaarsoles and 1,3-benzoxaarsoles has been explained[46] by their different aromatic stabilisations. In the case of the oxygen-containing heterocycles, the latter is lower owing to the greater amount of double bond character in the E=C bond.

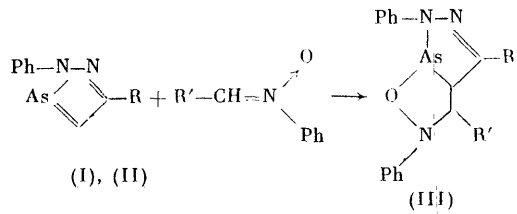
III. [2 + 3]Cycloaddition

Until recently, the first and only objects of the study [2 + 3]cycloaddition were 2*H*=1,2,3-diazaarsoles. In 1986, examples of [2 + 3]cycloaddition to 1*H*=1,2,4-diazaarsoles appeared.

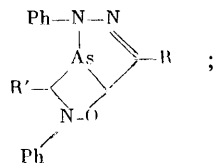
1. 2*H*-1,2,3-diazaarsoles

(a) Reactions with nitrones, nitrile oxides, and nitrile ylides

Cycloaddition to the $\lambda^3\sigma^2$As=C bond was achieved for the first time in the reaction of 2*H*=1,2,3-diazaarsoles (I) and (II) with nitrones:[48–50]



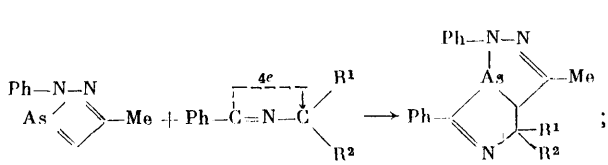
(I), (II) (III)



R=Me (I), R=Ph (II), R′=Ph, *p*-$NO_2C_6H_4$.

It has been established by X-ray diffraction[48] that, of the two possible isomers, 2,7-diphenyl-4-R-6-R′-1-arsa-2,3,7-triaza-8-oxabicyclo[3.3.0]oct-3-ene (III) is formed. Similar compounds based on 2*H*-1,2,3-diazaphosphole could not be obtained.

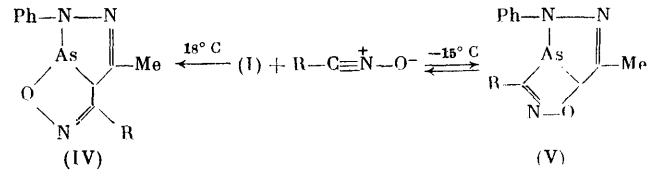
Carrie and co-workers showed that 2*H*-1,2,3-diazaarsoles as well as diazaphospholes react with nitrile oxides[51,62] and nitrile ylides[53] via the $\lambda^3\sigma^2$E=C bond. 2*H*-1,2,3-Diazaarsole (I) reacts with nitrile ylides to form one regioisomer:



(I)

R^1 = Ph, R^2 = H; R^1 = R^2 = H; R^1 = R^2 = Me.

Depending on the conditions, one or other regioisomer is formed in the case of nitrile oxides:



(IV) (V)

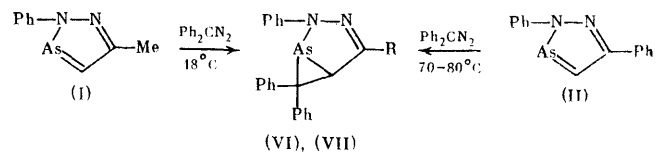
R=*p*-ClC_6H_4, t-Bu, Me, Ph.

The stable isomer (IV) was obtained at room temperature, while at −15 °C the product was the regioisomer (V). At room temperature in solution in toluene, the product (V) is converted quantitatively into compound (IV) via retrocycloaddition.

It may be that in the reaction of 2*H*-1,2,3-diazaarsoles with nitrones described above[48–50] the product (III) is also a thermodynamically controlled stable isomer, while its regioisomer could not be detected.

(b) Reactions with diphenyldiazomethane

The reaction of 2*H*-1,2,3-diazaarsoles (I) and (II) with diphenyldiazomethane leads to the bicyclic arsines (VI)[49] and (VII).[42,54] The formation of the arsirans (VI) and (VII) can be represented by the intial formation of the [2 + 3]cyclic adduct with the subsequent liberation of nitrogen. It has been demonstrated by a special experiment that diphenylcarbene does not afford the arsirans (VI) and (VII) on its reactions with diazaarsoles:

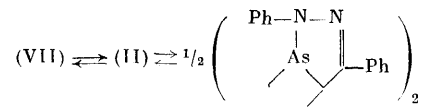


(I) (VI), (VII) (II)

R = Me(VI); R = Ph(VII).

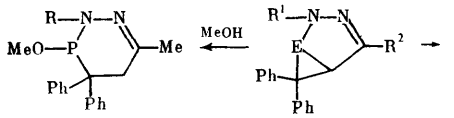
The diazaarsole (I) is more reactive in this reaction than the diazaarsole (II). Compounds (VI) and (VII) obtained are the first representatives of bicyclic arsirans. The structure of the product (VII) was established by X-ray diffraction.[55] Comparison of the X-ray diffraction data for the bicyclic compound (VI) and the analogous phosphorus-containing system[56] revealed a greater strain in the arsiran ring, which explains its lower stability.

The bicyclic arsiran (VII) is stable only when stored in the dark in the absence of solvents. In solutions at room temperature, it exists for 24 h. It then decomposes to diazaarsole (II), which dimerises:

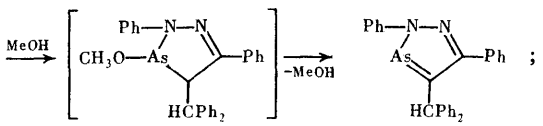


The difference between the strains in the arsiran and phosphiran rings is reflected in their different behaviour in relation to methanol. The addition of the alcohol to the phosphorus derivative (VIII) is accompanied by the dissociation of the inner P–C bond.[57] The addition of the alcohol to the bicyclic arsiran (VII) is apparently accompanied by the dissociation of the outer As–C bond with the subsequent liberation of the alcohol and the formation of 2,5-diphenyl-4-diphenyl-1,2,3-diaza-arsole. A new 2,4,5-trisubstituted 1,2,3-diazaarsole, whose structure was demonstrated by X-ray diffraction, has been obtained.[58] This is the first example of the $\lambda^3\sigma^3$As→$\lambda^3\sigma^2$As isomerisation in the series of diazaarsoles. In the

known [see, for example, Märkl[2] and Section (V) of the present review]:



(VII), (VIII)

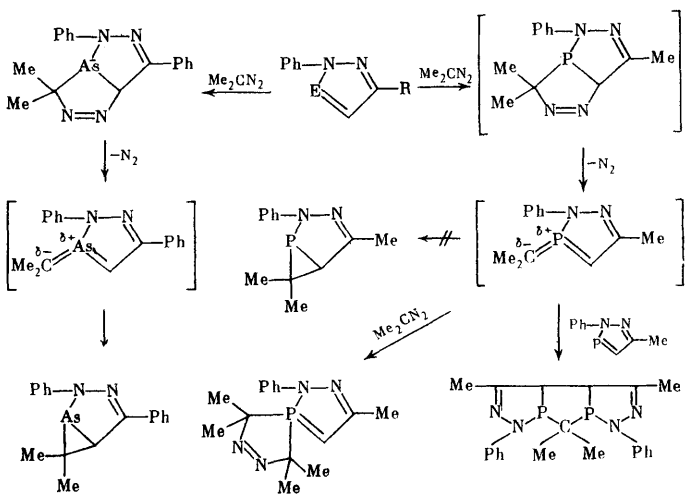


E = As(VII), P(VIII).

(c) Reactions with 2-diazopropane

Whereas 2*H*-1,2,3-diazaarsoles and 2*H*-1,2,3-diazaphospholes react with diphenyldiazomethane similarly to form stable bicyclic arsirans and phosphirans,[55,59] 2-diazopropane[60–66] introduced its characteristic features into these reactions. When 5-methyl-2-phenyl-1,2,3-diazaphosphole reacts with 2-diazopropane,[60–65] the closure to the phosphiran ring does not occur and the intermediate diazaphosphole ylide behaves both as a dipole and as a dipolarophile in the subsequent [2 + 3]cycloaddition reactions with both initial reactants: diazaphosphole and 2-diazopropane. As a result, reactions which led to previously unknown types of organophosphorus compounds were discovered.

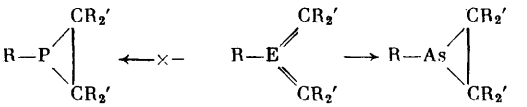
In the reaction with 2*H*-1,2,3-diazaarsole, 2-diazopropane[66] behaves similarly to diphenyldiazomethane. The final product is 2,4-diphenyl-6,6-dimethyl-1-arsa-2,3-diazabicyclo[3.1.0]hex-3-ene (IX). The bicyclic arsiran (IX) is formed via a crystalline cyclic adduct, detected at −70 °C. On further increase in temperature, the adduct evolves nitrogen and is probably converted into the product (IX) via a diylide:



(IX)

The results reported[67] for acyclic phosphorus and arsenic diylides are similar to those obtained in the reaction with 2-diazopropane.

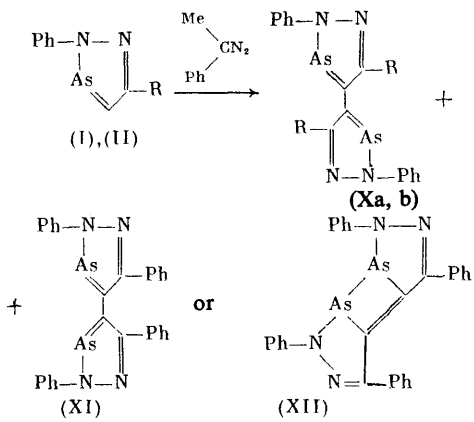
The arsenic diylide undergoes closure to the arsiran ring:



E = As, P; R = Ph, t-Bu; R′ = $SiMe_3$.

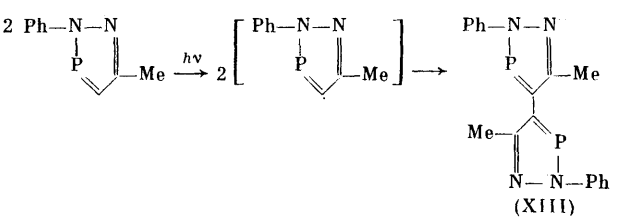
(d) Reactions with methylphenyldiazomethane

The reaction of 2*H*-1,2,3-diazaphospholes with methylphenyldiazomethane afforded in earlier studies[68,69] bicyclic phosphirans as two geometrical isomers. Similar isomers of bicyclic arsirans were not isolated in the reactions of 2*H*-1,2,3-diazaarsoles with the given diazo-compound. 1,4-Diarsabuta-1,3,-dienes (Xa, b) were obtained for the first time:[40]



R = Me (a), Ph (b).

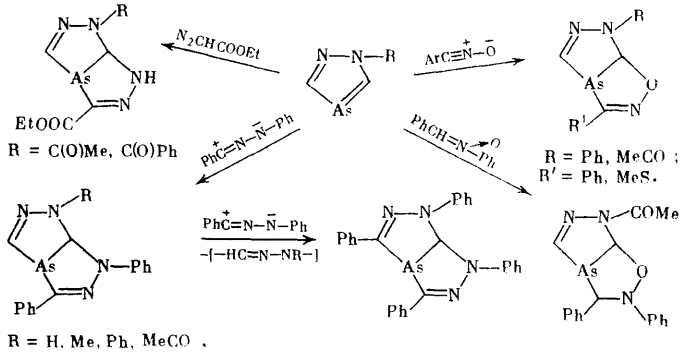
In addition, in the case of 2,5-diphenyl-1,2,3-diazaarsole (II) a second isomer, (XI) or (XII), was isolated. It could not be studied by X-ray diffraction owing to the insufficiently high quality of the crystals. *trans*-4,4′-Didehydrobis(5-methyl-2-phenyl-1,2,3-diazaarsole) (Xb) proved to be a full analogue (on the basis of X-ray diffraction data) of *trans*-4,4′-didehydrobis(5-methyl-2-phenyl-1,2,3-diazaphosphole) (XIII).[40,70,71] The data for the reactivity of diazaarsoles available at the present time, permit inferences about the mechanism of the formation of 1,4-diarsabuta-1,3-dienes (Xa, b). The phosphorus-containing product (XIII) was obtained under other conditions—on UV irradiation of 5-methyl-2-phenyl-1,2,3-diazaphosphole:



2. 1*H*-1,2,4-diazaarsoles

1*H*-1,2,4-Diazaarsoles enter under mild conditions into [2 + 3]-cycloaddition reactions with diazoacetic ester, nitrile imines, nitrile oxides, and nitrones.[41] It has been noted that the reactivity of *N*-acyl- and *N*-benzoyl-1,2,4-diazaarsoles is higher than that of the *N*-alkyl- and *N*-aryl-derivatives, which the authors explain by the reduced stabilisation of the aromatic system of the diazaarsole ring

in the acyl- and benzoyl-substituted compounds:



The [2 + 3]cycloaddition of nitrile oxides to 1*H*-1,2,4-diazaarsoles leads to a single regioisomer. In contrast to the reactions of 2*H*-1,2,3-diazaarsole (I) with nitrile oxides described previously,[51] the inversion of regioselectivity is not observed in this instance.

The reaction with diphenylnitrile imine results in the formation of cyclic adducts even at room temperature. At a higher temperature, they decompose to 1,3-diphenyl-1,2,4-diazaarsole. The latter enters again into the cycloaddition reaction with diphenylnitrile imine.

1-Acetyl-1,2,4-diazaarsole reacts with diphenyl nitrone to form a bicyclic adduct. It is of interest to note that the reactions of 2-phenyl-1,2,3-diazaarsoles (I) and (II) with diphenyl nitrone afforded in earlier studies[48–51] the product (III) with the opposite orientation of the nitrone relative to the $\lambda^3\sigma^2$As=C bond.

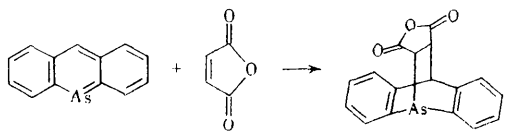
We did not encounter any data in the literature on the polarity of the $\lambda^3\sigma^2$As=C bond. Nevertheless, the formation of different regioisomers from 2*H*-1,2,3- and 1*H*-1,2,4-diazaarsoles and diphenyl nitrone shows that the regioselectivity of the addition to the As=C bond is determined not only by the charges on the atoms but also by the polarisability of the bond and the molecular-orbital characteristics of the reactants.

IV [2 + 4]cycloaddition

Depending on their structure, the $\lambda^3\sigma^2$As derivatives are capable of entering into the diene synthesis reaction as dienes and dienophiles.

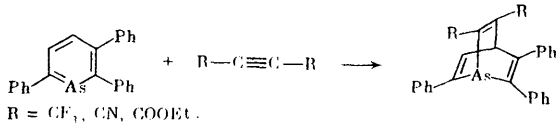
1. 9-Arsaanthracene

The unsubstituted 9-arsaanthracene exists only in solutions. After the addition of maleic anhydride, it gives rise to the [4 + 2]cyclic adduct.[33] This reaction was the first example of diene synthesis with participation of a $\lambda^3\sigma^2$As derivative:

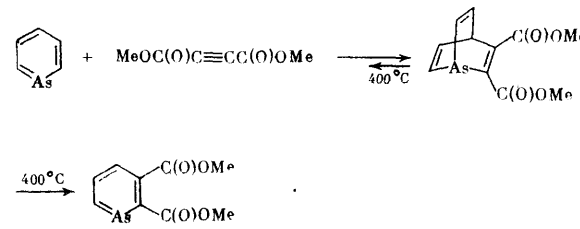


2. λ^3-Arsenins

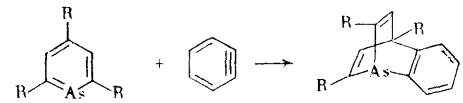
The reactivity of arsenins as dienes was first reported by Märkl:[72]



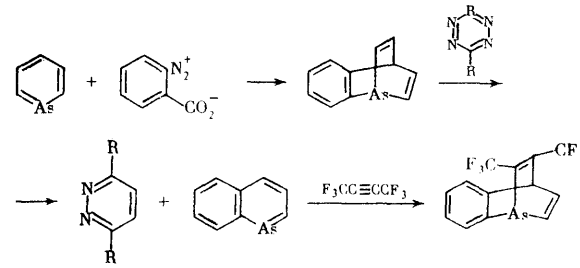
Arsenins exhibit a higher diene reactivity than phosphorins. In contrast to phosphorins, the [2 + 4]cycloaddition of dimethyl acetylenediacarboxylate to arsenins was achieved.[72–76] The thermal reversibility of the formation of arsabarrelenes was demonstrated in relation to the unsubstituted arsenin:[76]



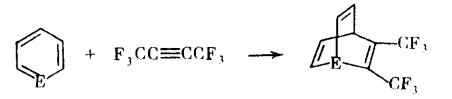
The 2,3-dimethoxycarbonylarsenin obtained at 400 °C enters into the diene synthesis reaction with arynes, which leads to benzarsabarrelenes:[72]



Ashe et al.[31] achieved a series of reactions during which [2 + 4]cycloaddition with participation of the $\lambda^3\sigma^2$As derivatives takes place: (1) reaction of arsenin with benzenediazonium-2-carboxylate and (2) reaction of 1-arsanaphthalene with hexafluorodimethylacetylene:



Comparison of the diene reactivities of benzene, pyridine, phosphorin, arsenin, antimonin, and bismin in relation to hexafluorobutyne showed[76] that the less electronegative the heteroatom in the ring the easier the Diels–Alder reaction:

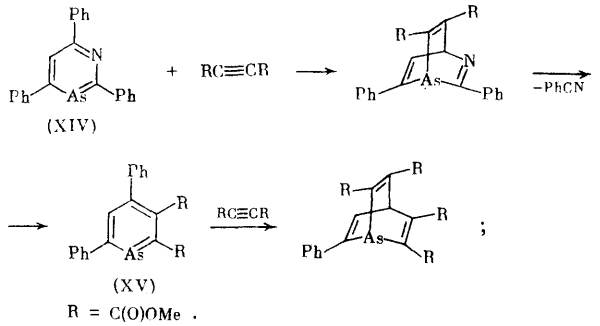


3. 1,3-Azaarsenines

The 1,3-azaarsenines synthesised by Märkl and Dietl[29] proved to be preparatively valuable.

2,4,6-Triphenyl-1,3-azaarsenine (XIV) enters into the Diels–Alder reaction with dimethyl acetylenedicarboxylate to form 1,3-azarsabarrelene, which decomposes during the reaction to the arsenin (XV). The latter is involved in a further diene synthesis reaction

with the initial dimethyl acetylenedicarboxylate:[77]



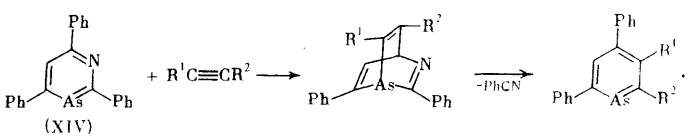
(XIV)

(XV)

R = C(O)OMe .

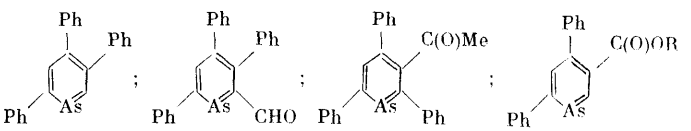
In contrast to the azaarsenine (XIV), the reaction of 2,4,6-triphenyl-1,3-azaphosphorine with acetylenedicarboxylate esters stops at the stage involving the formation of derivatives of $\lambda^3\sigma^2$P-phosphorins analogous to compound (XV). The phosphorins do not react further with acetylenedicarboxylate, which is consistent with the lower diene reactivity of phosphorins compared with arsenins.

1,3-Azaarsenines (XIV) react similarly with less reactive dienophiles. The azaarsabarrelenes obtained are converted into arsenins which do not enter into the Diels–Alder reaction:[77]



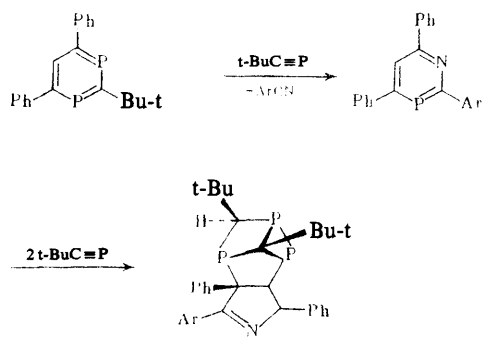
(XIV)

The following arsenins were obtained in this way:

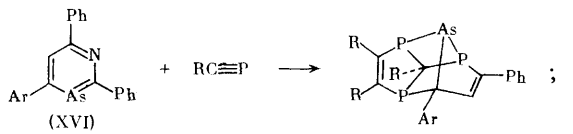


R = Me, H

Interesting data have been secured by Märkl and co-workers in the study of the reaction of 1,3-azaphosphorines[78,79] and 1,3-azaarsenines[80] with t-butyl-1-phosphaacetylene. 1,3-Azaphosphorines give rise to pentatetracyclic compounds in this reaction:



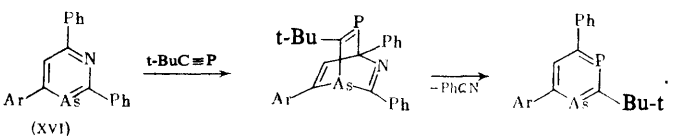
1,3-Azaarsenines (XVI) behave differently in this reaction: a compound with the 1,3-composition is formed. X-Ray diffraction analysis showed that the reaction product consists of a system comprising three five-membered and one four-membered ring:



(XVI)

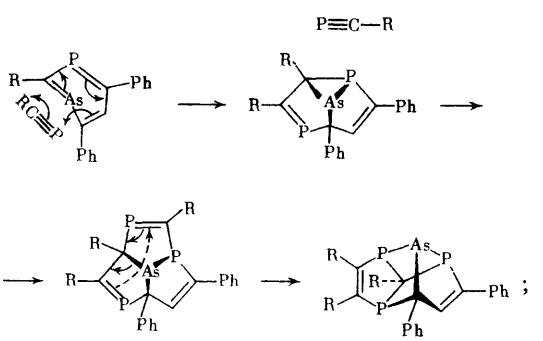
R = t-Bu.

The different behaviour of azaphosphorines and azaarsenines in this reaction has been explained[80] by the lower electrophilicity of the $\lambda^3\sigma^2$As atom in the azaarsenine compared with the electrophilicity of the $\lambda^3\sigma^2$P atom in the azaphosphorine, which leads to different mechanisms of their reactions. Whereas the reaction of the azaphosphorine with t-butylphosphaacetylene is induced by the nucleophilic attack of the acetylene *sp*-carbon atom on the $\lambda^3\sigma^2$P atom of the azaphosphorine in the case of the azaarsenine (XVI) the Diels–Alder reaction takes place initially. A phosphaarsabarrelene is formed. After the introduction of benzonitrile, it is converted into 1,3-phosphaarsenin:



(XVI)

The authors believe that the latter reacts with phosphaacetylene via the following mechanism:



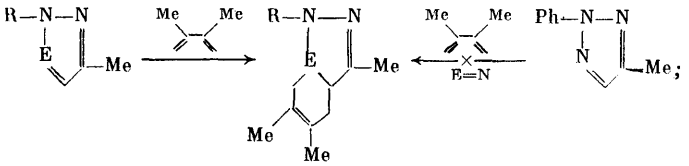
R = t-Bu.

Thus Märkl and co-workers carried out a brilliant series of studies in the field of diene synthesis involving six-membered $\lambda^3\sigma^2$P and $\lambda^3\sigma^2$As derivatives. The investigations led to new substituted λ^3-arsenins and λ^3-phosphorins. In addition the higher reactivity of arsenines compared with phosphorines in the Diels–Alder reaction was demonstrated and justified.

4. 2*H*-1,2,3-Diazaarsoles

We showed earlier[57] that 2*H*-1,2,3-diazaphospholes, which are derivatives of dicoordinated phosphorus, enter into the diene synthesis reaction with hexachlorocyclopentadiene. The ability of 2*H*-1,2,3-diazaarsoles to react with dienes was reported by Carrier and co-workers[81] in relation to the interaction with cyclopentadiene and 2,3-dimethylbutadiene. The reactivity of 5-methyl-2-phenyl-1,2,3-diazaarsole, 2,5-dimethyl-, 5-methyl-2-phenyl, and 2-acetyl-5-methyl-1,2,3-diazaphospholes, and 5-methyl-2-phenyl-1,2,3-triazole

in relation to 2,3-dimethylbutadiene were compared:

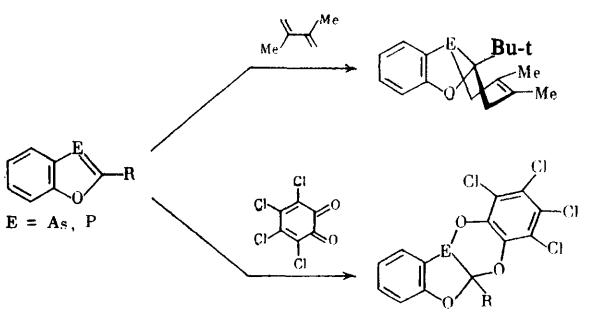


E = P, R = MeCO, Ph; E = As, R = Ph (I).

2-Acetyl-5-methyl-1,2,3-diazaphosphole and 5-methyl-2-phenyl-1,2,3-diazaarsole are the most reactive in this reaction. Cyclic adducts with 2,5-dimethyl-1,2,3-diazaphosphole and the corresponding triazole were not obtained. The absence of the reaction between the triazole and 2,3-dimethylbutadiene clearly demonstrates the greater reactivity of the $\lambda^3\sigma^2P=C$ and $\lambda^3\sigma^2As=C$ bonds compared with the $\lambda^3\sigma^2N=C$ bond in the reactions considered.

5. 1,3-Benzoxaarsoles

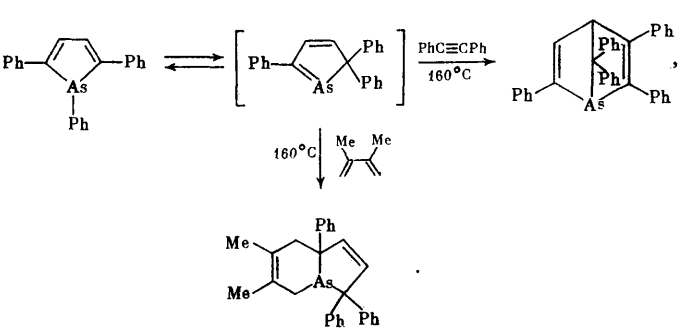
1,3-benzoxaarsoles and 1,3-benzoxaphospholes react [82] with 2,3-dimethylbutadiene and tetrachloro-*o*-benzoquinone to form [2 + 4]-cyclic adducts. The $\lambda^3\sigma^2As$ derivative is more reactive in these processes than the $\lambda^3\sigma^2P$ compound.



R = Me, t-Bu.

6. 2,5,5-Triphenylarsole

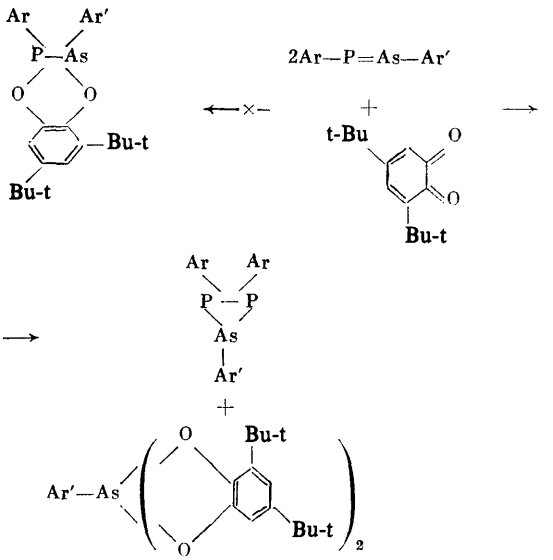
At a high temperature, 1,2,5-triphenylarsole isomerises to 2,5,5-triphenylarsole, which enters into the Diels–Alder reaction both as a diene (in the reaction with tolane) and as a dienophile (in the reaction with 2,3-dimethylbutadiene):[37]



Similar results were obtained for a phosphorus-containing compound — 1-phenylphosphole.[37] The Diels–Alder reaction proceeds more readily with arsoles than with phospholes, because, according to the authors, the lone pair of the arsenic atom is less reactive than that of the phosphorus atom.

7. Phosphaarsaethylenes

Data on reactions involving cycloaddition to acyclic $\lambda^3\sigma^2As$ compounds are almost absent in the literature. There is a communication[83] stating that an attempt to obtain the [2 + 4]cyclic adduct by the reaction of *P*-(2,4,6-tri-t-butylphenyl)-*As*-(2,4,6-tri-isopropylphenyl)phosphaarsaethylene with 3,5-di-t-butyl-*o*-benzoquinone was unsuccessful, diphosphaarsiran and arsine being obtained:

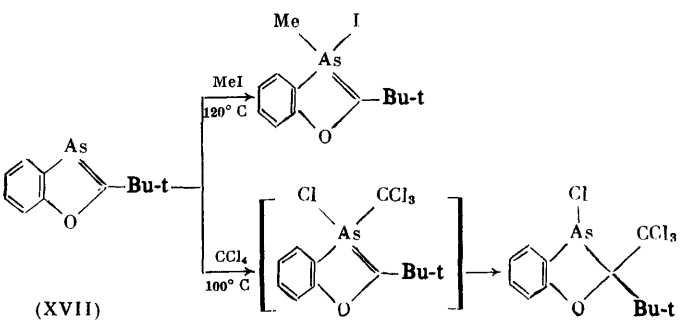


V. Aromaticity

The chemical properties described above (Sections II–IV) characterise $\lambda^3\sigma^2As$ compounds as systems related to unsaturated compounds. However, individual representatives of cyclic derivatives of dicoordinate arsenic exhibit also the properties of aromatic systems.

1,3-Benzaza- and 1,3-benzoxa-arsoles and 1,3-benzaza- and 1,3-benzoxaphospholes can be classified as aromatic compounds in terms of the nature of the delocalisation of the π-electrons (according to UV-spectroscopic and X-ray diffraction data).[84,85] X-Ray diffraction data for unsubstituted benzazaarsole[84] (bond lengths, bond angles, and planarity of the molecule) indicate the aromaticity of the latter. Comparison of the structural parameters of benzimidazole, benzazaphosphole, and benzazaarsole demonstrated their electronic and structural similarly.[85]

2-t-Butyl-1,3-benzoxaarsole (XVII) exhibits a low reactivity in relation to electrophiles. However, under severe conditions it reacts with MeI to form λ^5-1,3-benzoxaarsole:[46]

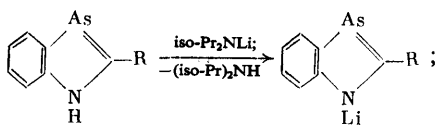


(XVII)

The reaction with CCl_4 proceeds differently. The primary 1,1-adduct rearranges under these conditions to λ^3-dihydrobenzoxaarsole.

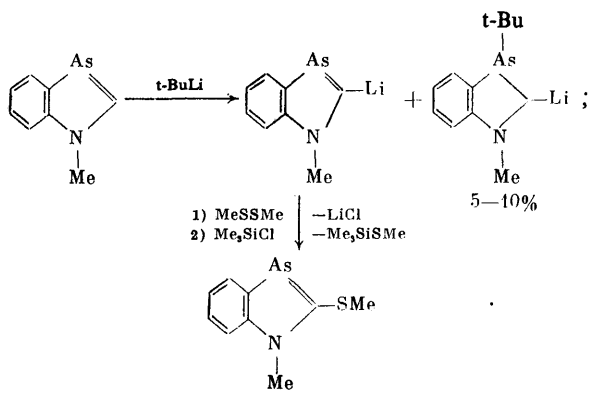
1,3-Benzoxaarsole and 2-t-butyl-1,3-benzoxaphosphole do not react with "hard" bases,[46] which also indicates their aromaticity.

The metallation of 2R-1,3-benzazaarsoles[47] takes place in the 1-position in the azaarsole ring:

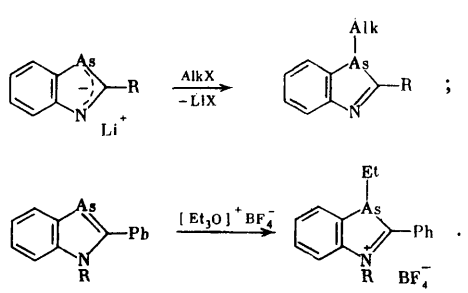


R = H, Me, t-Bu, iso-Pr.

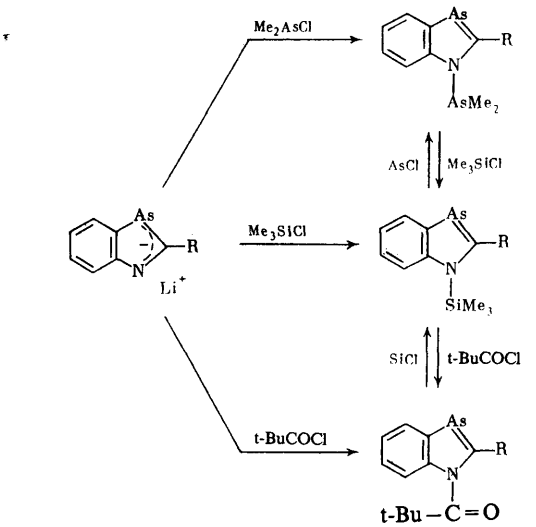
In contrast to unsubstituted 1,3-benzazaarsole, which reacts with t-butyllithium via the 1,2-addition mechanism, 1-methyl-1,3-benzazaarsole is metallated by t-butyllithium in the 2-position. The metallation product reacts with dimethyl disulphide, forming 1-methyl-2-methylthio-1,3-benzazaarsole:



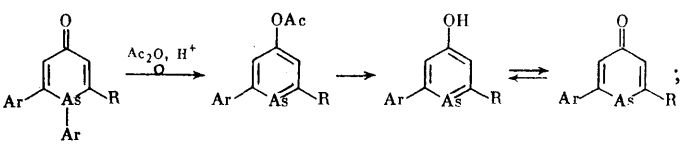
Whereas unsubstituted 1,3-benzaazaarsole does not react with MeI,[86] substituted 1,3-benzazaarsoles are alkylated[47] at the arsenic atom:



An interesting chain of substitutions has been achieved by Heinicke et al.:[47]

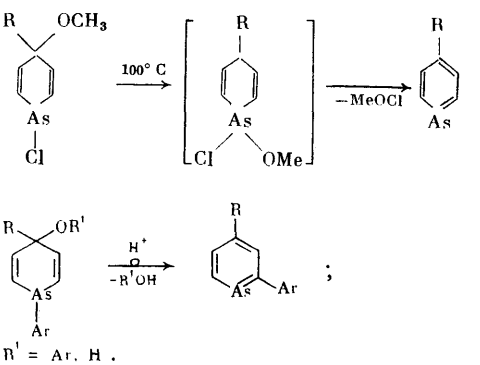


The properties of aromatic systems are also shown by representatives of another class of $\lambda^3\sigma^2$As compounds—arsenins. Thus 1-aryl- and 1,2-diaryl-arsacyclodienones[87,88] in acetic anhydride undergo, in the presence of a catalytic amount of H_2SO_4, the arsacyclohexadienone-arsaphenol rearrangement, corresponding to the rearrangement in the aromatic series, forming 2-aryl-6R-4-hydroxyarsenin. Alkaline hydrolysis of the latter gives rise to 2,6-diarylarsacyclodien-4-ones, which exist in solution in equilibrium with their enolic forms. In contrast to the 2,6-disubstituted 4-hydroxyarsabenzenes unsubstituted 4-hydroxyarsabenzene[89] exists exclusively in the enolic form and there is no tautomeric conversion into the cyclodienone.



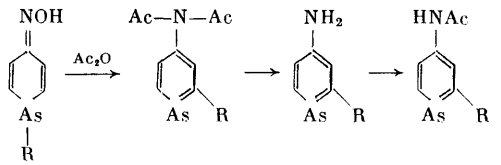
R = Ar, H .

The conversion of $\lambda^3\sigma^3$As derivatives into $\lambda^3\sigma^2$As compounds, which are more conjugated systems,[2,88,90,91] is known to occur in a number of instances:

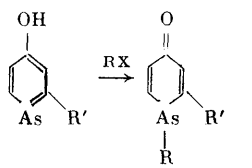


R' = Ar, H .

An interesting series of transformations was achieved by Märkl and Rampal[92] in the oxime–aminoarsenin series:

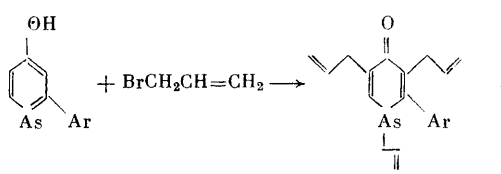


4-Hydroxyarsenins[87] are alkylated preferentially in the hydroxy-group with the subsequent migration of the alkyl substituent to the arsenic atom:



R′ = Ar, H; X = I, Br .

In the reaction of 2-aryl-4-hydroxyarsenin with 3-bromopropene, substitution in the arsabenzene ring also takes place:

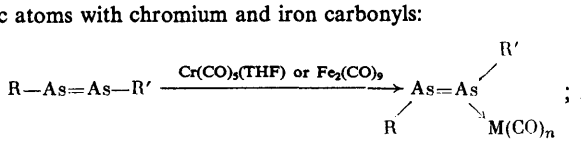


Among the chemical properties of arsinines considered (Sections IV and V), one may note their dual reactivity. On the one hand, they enter into the diene synthesis reaction as dienes and on the other they undergo reactions characteristic of aromatic compounds. Admittedly, both types of reactions characterise arsinines as conjugated systems. The ability of arsinines to enter into complex formation reactions (see the next Section) involving the $\lambda^3\sigma^2$As atom as well as the entire π-system also indicates the wide variety of their properties.

VI. Complex formation

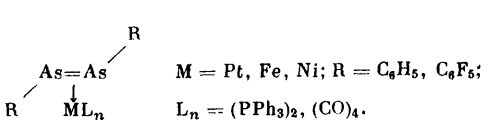
There are some data on the complex formation reactions of derivatives of dicoordinate arsenic. They are partly included in a review article.[7] So far η^1-, η^2-, and η^6-complexes of $\lambda^3\sigma^2$As compounds are known.

Diarsenes[93,94] are capable of forming η^1-complexes via one of the arsenic atoms with chromium and iron carbonyls:

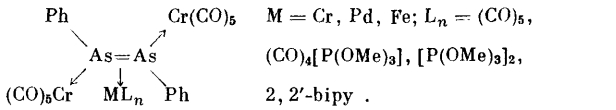


R = 2, 4, 6-(t-Bu)$_3$C$_6$H$_2$, R′ = (Me$_3$Si)$_2$CH.

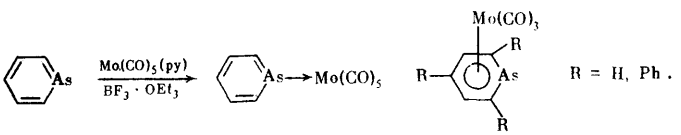
The η^2-complexes of diarsenes have been obtained:[94–97]



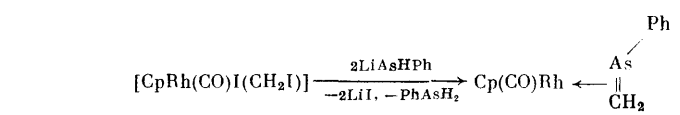
Diphenyldiarsene can enter into the complex formation reaction involving both the double bond and the arsenic atoms,[98–100] forming the following compounds:



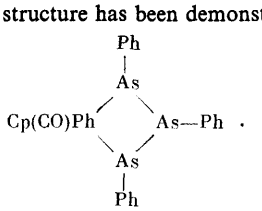
In the case of λ^3-arsenin, the η^1-complexes[101] and the η^6-complexes[101,102] are known:



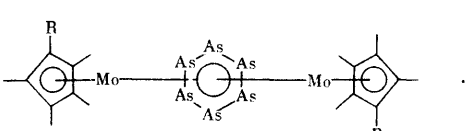
It has been noted that complex formation promotes the stabilisation of $\lambda^3\sigma^2$As atoms. Thus phenylarsene Ph–As=CH$_2$ does not exist in a free state but its η^2-complex has been obtained:[103,104]



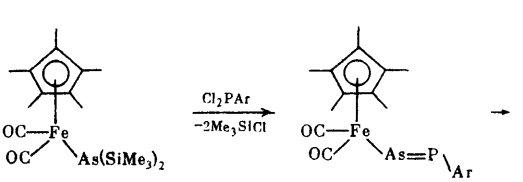
On recrystallisation, the latter is partly converted into a compound whose structure has been demonstrated by X-ray diffraction:



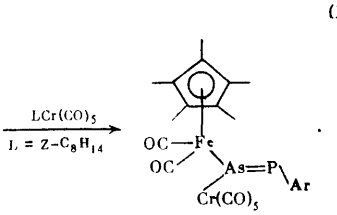
Hexaarsabenzene is known[30] at the present time only in the form of η^6-complexes:



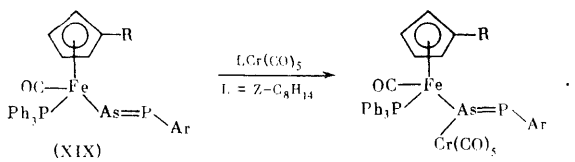
The formation of the phosphaarsene (XVIII) has been detected spectroscopically in the reaction mixture and its complex has been isolated.[105,106] The structure of the latter has been demonstrated by X-ray diffraction:



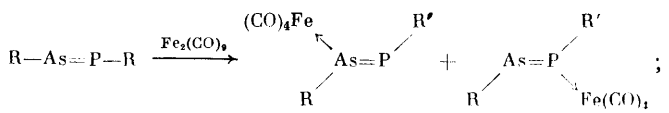
(XVIII)



In contrast to compound (XVIII), the phosphazaarsene (XIX) is stable. Its reaction with $Cr(CO)_3$ afforded[107] an η^1-complex:

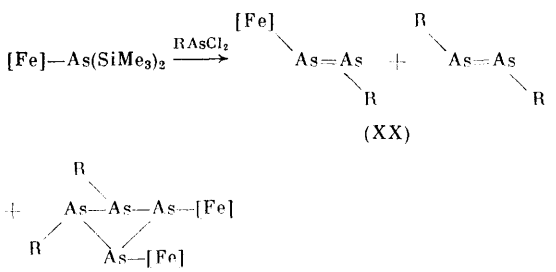


Phosphaarsenes are capable of forming complexes not only via the $\lambda^3\sigma^2$As atom but also via the $\lambda^3\sigma^2$P atom. A mixture of such complexes has been obtained.[108,109] They could not be separated, but they were identified spectroscopically by $^{31}P\{^1H\}$ NMR:



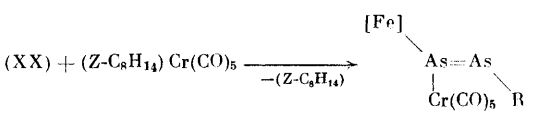
$R = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$, $R' = (Me_3Si)_2CH$.

The synthesis of the diarsene (XX) [26] is not ambiguous, in contast to the analogous synthesis of the phosphaarsene (XVIII):



$[Fe] \equiv (\eta^5\text{-}C_5Me_5)(CO)_2Fe$; $R = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$.

Compound (XX) is unstable, but its $Cr(CO)_5$ derivative proved to be stable:



- - - o 0 o - - -

The experimental data examined in this review indicate the high reactivity of $\lambda^3\sigma^2$As derivatives. The wide variety of the properties shown by these compounds opens a route to various chemical reactions, new types of reactions, and the synthesis of new organoarsenic compounds. Further study of the chemical properties of dicoordinate arsenic is therefore of current interest.

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