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The Stereochemistry of Organoarsenic Compounds

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The structure of organic compounds of arsenic is considered. Data are presented on the configurational stability and the energy of the inversion barrier in asymmetric arsines. The methods of synthesis of tertiary asymmetric arsenic compounds are surveyed. The results of the separation of asymmetric arsines into optically active isomers and the mechanisms of their transformation as well as the influence of substituents in the benzene ring on the optical activity are described. An analogy is drawn between the stereochemistries of organophosphorus and organoarsenic compounds.
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I. INTRODUCTION

The stereochemistry of organoelemental compounds, which has been developing vigorously recently, is being gradually transformed into an independent section of organic chemistry. This field of stereochemistry is important for the understanding of the general characteristics of optical isomerism and stereochemical transformations, and also in the study of reactivity and reaction mechanisms. Stereochemical problems, particularly those which are associated with the reactions of optically active compounds, have been occupying an increasingly important place in research on the mechanisms of organic reactions. The study of the structure and the chemical and optical properties of asymmetric arsines is one of the urgent problems in this connection.

The number of publications dealing with problems of the stereochemistry of organoarsenic compounds has increased appreciably recently. However, so far there has been no complete compilation of the literature reflecting the state of research in this field during the latest period. The present paper surveys and considers in detail data concerning the structure, methods of synthesis, and the stereochemistry of organoarsenic compounds. Our aim was not an all-embracing discussion of the problem and we endeavoured to concentrate attention on asymmetric arsenic compounds which have been studied systematically recently. In certain cases a comparison is made with the analogous phosphorus compounds.

II. THE STRUCTURE OF ARSENIC COMPOUNDS

As representatives of Group V in the Periodic System, phosphorus and arsenic exhibit certain analogies in the structure of their electron shells. In contrast to its closest analogue—phosphorus in the Third Period, arsenic, which is an element in the Fourth Period, has a completed M shell and an incomplete N electron shell. The following electronic configurations correspond to neutral phosphorus and arsenic atoms:

$$P—1s^2 2s^2 p^6 3s^2 p^3;\quad As—1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^3.$$

In neutral phosphorus and arsenic atoms the outer energy levels are not fully occupied by electrons: they contain two electrons with antiparallel spins in the s orbital and only one electron in each of the three p orbitals. The $3d$ orbital in phosphorus atoms and the $4d$ and $4f$ orbitals in arsenic atoms are unoccupied. It is assumed[1] that these orbitals are used in the formation of bonds in the maximum-valence phosphorus and arsenic compounds. Their $4s$, $4p$, and $3d$ orbitals are most available as regards energy for the formation of chemical bonds[2]. Phosphorus and arsenic atoms in their various compounds can be surrounded by between three and six substituents[3].

Within the framework of the present review, organic derivatives of tervalent arsenic as well as individual representatives of quinquevalent arsenic having the structures

$$R_3As,\ R_3As{=}O,\ R_3As{=}S,\ \text{and}\ [R_4As]^{\oplus}X^{\ominus}$$

are considered in greatest detail.

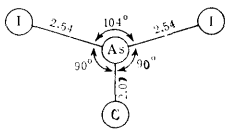
In compounds phosphorus and arsenic atoms have the following electronic configurations: p^3, sp^3, sp^3d, and sp^3d^2. Certain tervalent phosphorus and arsenic compounds, for which the p^3 structure has been postulated, are stable under the usual conditions[4,5]. Examples are provided by phosphine PH_3 and arsine AsH_3. Spectroscopic studies have shown that the hydrogen atoms in the PH_3 and AsH_3 molecules are equivalent and that the H–P–H and H–As–H valence angles are 94° and 92° respectively[6,7]. These angles are greater by 4° in phosphine and 2° in arsine than the angle formed by the overlap of pure p orbitals (90°). Hence it follows that the H–P and H–As bonds are formed with an appreciable involvement of p orbitals and that the lone electron pair is localised predominantly in the s orbitals of phosphorus and arsenic atoms.

Spectroscopic data[7-10] have shown that the replacement of hydrogen by a halogen, alkyl, or aryl in tervalent phosphorus and arsenic compounds leads to an increase of valence angles. The relative content of lone electron pairs of the p type in these compounds increases. The valence angles in trimethyl and trifluoro-derivatives of phosphorus and arsenic increase to 99° and 96° and to 104° and 102° respectively.

The valence angles in certain tervalent phosphorus and arsenic compounds show that there is no significant difference between the types of hybridisation of the lone electron pair orbitals in phosphorus and arsenic. The content of lone electron pairs of the p type in tertiary phosphines and arsines varies near 50%, while in secondary and primary phosphines and arsines it is much less[11]. With

increase of the *p* character of the lone electron pairs, there is also an increase of the capacity of the hybrid lone pair for p,π conjugation [11].

Comparison of the lengths and energies of arsenic–halogen bonds [10,12–21] shows that shortest and strongest bonds are observed for the F substituent. On passing to Cl, Br, and I, the lengths of the bonds with arsenic increase and there is a corresponding decrease of the dissociation energy. The structure of primary halogenoarsines has been studied in relation to difluoromethyl- and di-iodomethyl-arsines (I). The valence angles and intra-atomic distances have been determined by a microwave spectroscopy [22,23].

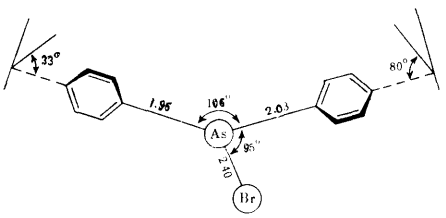


(I)

Among unsaturated compounds, the structure of β-chlorovinyldichloroarsine has been studied by electron diffraction [24]. Appreciable differences in the C–As–Cl valence angles and As–Cl distances relative to saturated compounds were not observed, except that the As–C bond length is reduced (to 1.90 Å). Secondary halogenoarsines were also studied by electron diffraction. In these compounds the C–As–X bond lengths and the valence angle are influenced by the nature of the substituent.

It has been shown [15] that the As–C bond lengths in halogenodimethylarsines $(CH_3)_2As–X$ (where X = Cl, Br, or I) are approximately the same (1.98 Å). The C–As–Cl and C–As–I valence angles are similar, while the C–As–Br valence angle (96°) is smaller than in chloro- and iodo-arsines. The C–As–C valence angle is 96°. [25–27]

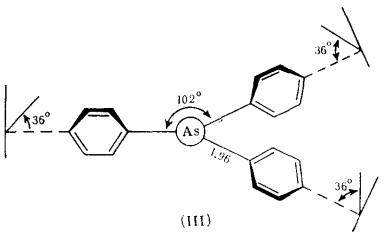
The C–As bonds linking the two aromatic groups in diarylhalogenoarsine molecules are not the same [19,21]. The C–As bond lengths in $(C_6H_5)_2As–Br$ (II) are 1.96 and 2.03 Å. The C–As–C and C–As–Br valence angles are 106° and 95° respectively. The As–Br interatomic distance (2.40 Å) is shorter than in alkylhalogenoarsines. The benzene rings in bromodiphenylarsine are inclined at different angles to the base of the pyramid. Their planes make angles of 33° and 80° with the plane of the base.



(II)

In the series of tertiary aliphatic arsenic derivatives the structure of trimethylarsine $As(CH_3)_3$ has been thoroughly investigated. It has been established by electron diffraction, X-ray diffraction, and microwave spectroscopy [15,27,28] that all the As–C bonds in trimethylarsine are equivalent. The As–C interatomic distances are equal (1.98 Å) and the C–As–C valence angles are the same and amount to 96°.

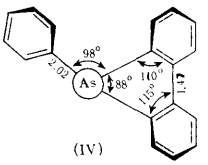
Among aromatic derivatives of tervalent arsenic, the structures of tritolyl arsine (III) and trixylylarsine have been most thoroughly investigated [10,26,29]. The molecules have identical symmetries, similar As–C bond lengths (1.96 and 1.99 Å), and equal (102°) C–As–C valence angles.



(III)

The benzene rings in crystalline tritolyl- and trixylyl-arsines are located in the plane of the base of the molecule at approximately the same angles, which are 36° and 37° respectively.

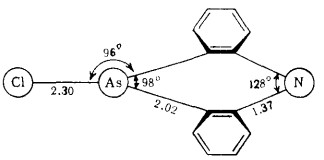
Among cyclic tervalent arsenic compounds, the molecule of 9-phenyl-9-arsafluorene (IV) has been thoroughly investigated.



(IV)

The C–As–C valence angle in the ring is 88°. The length of the C–C bond between the aromatic rings is 1.47 Å. These rings are located in one plane, while the isolated phenyl group is almost perpendicular to it. Its C–As–C valence angle is greater by 10° than the endocyclic angle and the As–C interatomic distances are 2.02 Å.

Among tervalent arsenic compounds with a six-membered ring, the molecule of 10-chloro-5,10-dihydrophenarsazine (V) has been investigated [31].



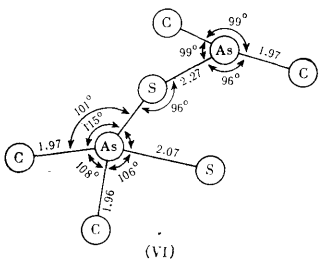
(V)

The three condensed rings do not lie in one plane. The angle of the bend along the As–N axis is 169°. The As–Cl interatomic distance (2.30 Å) is somewhat greater than in $(C_6H_5)_2As–Cl$. The C–N–C angle (128°) is greater than the analogous C–As–C angle (98°). According to Camerman and Trotter [31], the characteristic feature of the molecular structure of this compound can be explained by the interaction of the π electrons of the phenyl groups with the free electron pair of nitrogen and the *d* orbital of arsenic.

Tetracoordinate arsenic derivatives—sulphides (As=S), oxides (As=O), and arsonium compounds $(=As=)^+X^-$—have a tetrahedral configuration. It has been suggested that $p_\pi–d_\pi$ conjugation is characteristic of the corresponding As=O and As= bonds [32,33].

The two arsenic atoms in the cacodyl disulphide (VI) molecule [34] are in different valence states (As^{III} and As^{V}). Apart from the three substituents surrounding the central

atom, the tetracoordinate arsenic atom has a fourth substituent—sulphur. The C–As=S valence angle is 106° and the As=S bond length (2.07 Å) approaches the As–C bond length (1.96 Å). The C–As–C valence angles are 108°, being similar to the analogous C–As–S angle (106°). The average lengths of all the bonds and all the valence angles in this compound approach the parameters characteristic of a tetrahedral structure.



(VI)

In compounds of quinquevalent phosphorus and arsenic, where the central atom is surrounded by four substituents one of which is linked to it by a double bond, a tendency appears towards the formation of new types of asymmetric molecules. It has been suggested[35] that in compounds of this kind one encounters a new geometrical model, which consists of a distorted tetrahedron with a single double bond directed to one of the vertices. If the three remaining substituents are different, then the molecule has no symmetry plane. Hence it follows that the molecules corresponding to this model are asymmetric and exist in the form of two sterically incompatible optically active isomers. The problem of the optical activity of these compounds is discussed below.

III. METHODS OF SYNTHESIS OF CHIRAL ORGANOARSENIC COMPOUNDS

1. The use of Organometallic Compounds

Of the existing methods of synthesis of tertiary arsines, in the present review we shall consider only those which are used most frequently to synthesise chiral organoarsenic compounds. The commonest method involves the interaction of secondary organoarsenic halides with organic derivatives of Group I, II, and IV metals. In this method sodium can be successfully replaced by other metals: Li, K, Mg, Zn, and Hg.[36-57] Organozinc and organomercury compounds have been recently displaced to an increasing extent by the more readily available and effective for comparative purposes lithium compounds and Grignard reagents[58,59].

When organomagnesium compounds are used, the reaction is usually carried out in ether. Benzene, iso-octane, and tetrahydrofuran are sometimes used successfully. The yield of the required products increases when arsenic iodide compounds are employed[60]. Preliminary dilution of halogenoarsines with dry petroleum ether[61] or benzene[62] also increases the yield of tertiary arsines. Various chiral alkylarylarsines have been synthesised by this method[63-66]:

$$\begin{matrix}\mathrm{Alk}\\ \mathrm{Ar}\end{matrix}\!\!>\!\mathrm{AsCl} + \mathrm{RMgHal} \rightarrow \begin{matrix}\mathrm{Alk}\\ \mathrm{Ar}\end{matrix}\!\!>\!\mathrm{AsR} + \mathrm{MgHalCl} \quad .$$

Under the conditions of the Grignard reaction, chiral arsines can be obtained in high yields by treating a mixture of two Grignard reagents with alkyl- and aryldichloroarsines[67]. Isopropylmethylphenylarsine, for example, was obtained in this way:

$$\mathrm{C_6H_5{-}As}\!\!<\!\!\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix} + \mathrm{CH_3MgI} + \text{iso-}\mathrm{C_3H_7MgBr} \xrightarrow{\text{ether/THF}} \text{iso-}\mathrm{C_3H_7{-}As}\!\!<\!\!\begin{matrix}\mathrm{CH_3}\\ \mathrm{C_6H_5}\end{matrix} \quad .$$

The reaction involves the formation of a certain amount of symmetrical arsines. In many instances the method can be more effective than the existing multistage syntheses. The reaction of halogenoarsines with Grignard reagents is used as the principle method for the synthesis of tertiary aliphatic and aromatic arsenic derivatives[68]. Apart from halogenoarsines, the corresponding arsine oxides[69], aminoarsines[70], and arsinic acid esters[71] react similarly with Grignard reagents:

$$\begin{matrix}\mathrm{RO}\\ \mathrm{R'O}\end{matrix}\!\!>\!\mathrm{As{-}OR} + \mathrm{R''MgCl} \rightarrow \begin{matrix}\mathrm{RO}\\ \mathrm{R'O}\end{matrix}\!\!>\!\mathrm{As{-}R''} + \mathrm{ROMgCl} \quad .$$

Grignard reagents are most convenient not only for the synthesis of aliphatic or aromatic arsenic compounds but also for the synthesis of certain other tertiary arsines[72-77], including unsaturated arsines[78-87].

There exist a series of special methods for the synthesis of chiral arsines and their analogues, examples of the use of which are not numerous. They include in the first place the Wurtz–Fittig reaction, which consists in the interaction of halogeno-substituted organoarsenic derivatives with alkyl halides or aryl halides in the presence of metallic sodium. In the field of organoarsenic compounds it is known as the Michaelis condensation[88], Michaelis having used it to synthesise triarylarsines and mixed arsenic compounds without functional groups in the chain. It has been suggested[89] that an intermediate is formed with an As–Na bond, which leads to a tertiary arsine on interaction with an alkyl or aryl halide:

$$\mathrm{RR'As{-}Hal} + 2\mathrm{Na} \leftrightarrow \mathrm{RR'As{-}Na} + \mathrm{NaHal} \quad ,$$
$$\mathrm{RR'As{-}Na} + \mathrm{Hal{-}R''} \rightarrow \mathrm{RR'AsR''} + \mathrm{NaHal} \quad .$$

The yield of the final product is independent of the nature of the halogen, the form of sodium employed playing a more important role[90]; the highest yield is obtained with dispersed sodium[91]. The reaction is carried out in dry benzene, toluene, or ether and is catalysed by ethyl acetate. It is normally used to synthesis triaryl- or alkylaryl-arsines[92-99].

The allyl esters of asymmetric arsinous acid have been synthesised by the reaction of ethylphenylarsine oxide with allyl alcohol[87]:

$$\left(\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{C_6H_5}\end{matrix}\!\!>\!\mathrm{As}\right)_2\mathrm{O} + 2\mathrm{HOCH_2{-}CH{=}CH_2} \rightarrow 2\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{C_6H_5}\end{matrix}\!\!>\!\mathrm{As{-}OCH_2CH{=}CH_2} + \mathrm{H_2O} \quad .$$

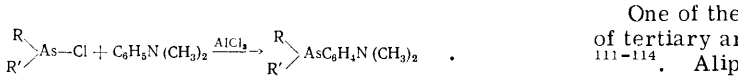
A new method of synthesis of chiral arsines[67] is based on the ability of arsonium salts to alkylate triphenylphosphine:

$$\mathrm{C_6H_5AsCl_2} \xrightarrow[-\mathrm{MgHalCl}]{+2\mathrm{C_6H_5CH_2MgHal}} \mathrm{C_6H_5As(CH_2C_6H_5)_2} \xrightarrow{+\mathrm{RHal}}$$
$$\rightarrow \left[\begin{matrix}\mathrm{C_6H_5CH_2}\\ \mathrm{C_6H_5CH_2}\end{matrix}\!\!>\!\mathrm{As}\!\!<\!\!\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{R}\end{matrix}\right]^{\oplus}\mathrm{Hal}^{\ominus} \xrightarrow[[(\mathrm{C_6H_5})_3\mathrm{PCH_2C_6H_5}]^{\oplus}\mathrm{Hal}^{\ominus}]{(\mathrm{C_6H_5})_3\mathrm{P}} \mathrm{R{-}As}\!\!<\!\!\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CH_2C_6H_5}\end{matrix};$$
$$\mathrm{R}=\mathrm{CH_3},\ \mathrm{C_2H_5},\ \mathrm{C_3H_7},\ \text{or n-}\mathrm{C_4H_9};\ \mathrm{Hal}=\mathrm{Br}\ \text{or}\ \mathrm{I}.$$

The reaction proceeds under mild conditions in dimethylformamide. The yields of tertiary arsines are nearly quantitative.

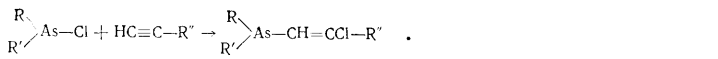
Tertiary arsines have been obtained in fairly high yields by the condensation of secondary chloroarsines with aromatic hydrocarbons in the presence of aluminium

chloride[100,101]. The presence of electron-donating groups in the aromatic ring facilitates the condensation:

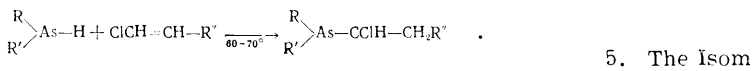


2. Syntheses with Participation of Mobile Atoms

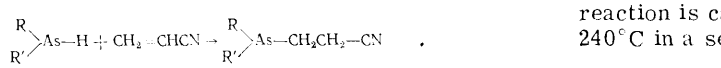
Tertiary arsines with triple carbon–carbon bonds have been synthesised[102] by the direct interaction of acetylene derivatives with halogenoarsines under ultra violet irradiation:



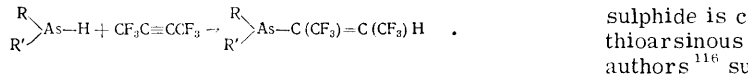
Secondary arsines readily add to chlorine- and fluorine-containing unsaturated hydrocarbons[103–107]. This reaction leads to the formation of tertiary asymmetric arsines in a high yield:



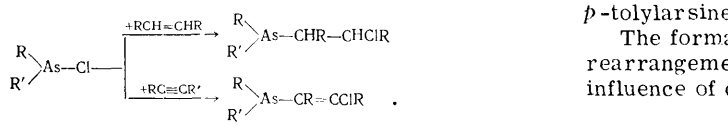
It has been shown[105] that, owing to the mobility of hydrogen, secondary arsines add smoothly to acrylonitrile in the presence of bases with formation of the corresponding chiral arsinonitriles:



The addition of secondary arsines to acetylenic hydrocarbons has been studied in relation to a limited number of examples. It has only been shown that the reaction proceeds readily with formation of tertiary ethylene derivatives of arsenic[102]:

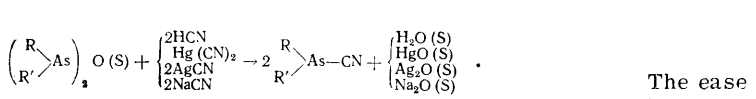


Asymmetric arsines have been obtained[103] by the analogous reaction of secondary halogenoarsines with ethylenic and acetylenic hydrocarbons after prolonged heating at 180°C:



3. Syntheses Based on Hydrocyanic Acid Derivatives

The asymmetric derivatives of tervalent arsenic containing the cyano-group are of interest for the investigation of stereochemical properties. Hydrolysis of arsinonitriles leads to the corresponding carboxy-derivatives of arsenic. The synthesis of tertiary arsines containing a cyano-group linked directly to the arsenic atom is achieved by the interaction of secondary arsine oxides or sulphides with hydrocyanic acid and mercury, silver, and alkali metal cyanides[108–110]:

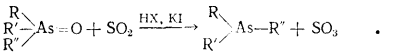


The same compounds can be obtained in high yields also from secondary halogenoarsines[108–110].

4. The Reduction of Arsine Oxides

One of the most convenient methods for the preparation of tertiary arsines involves the reduction of their oxides[111–114]. Aliphatic, aromatic and mixed arsines are obtained by this procedure.

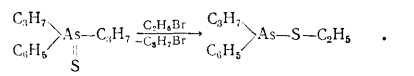
When tervalent arsenic oxides containing three different hydrocarbon groups are reduced, chiral arsines are formed. The reaction is carried out in an acid medium. The reducing agents most frequently employed are sulphur dioxide and tin and the acids are hydrochloric and phosphoric:



The yields of desired products are almost quantitative. When arsine oxides are reduced by sulphur dioxide in hydrochloric acid, an alcoholic solution of iodine or a potassium iodide solution are used as catalysts.

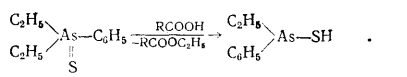
5. The Isomerisation Reaction

Asymmetric compounds containing the =As–S–R linkage are obtained by a rearrangement of alkylarylarsine sulphides on interaction with alkyl halides[115]. The reaction is carried out by heating the reactants at 100 to 240°C in a sealed tube without a solvent for 7–25 h:

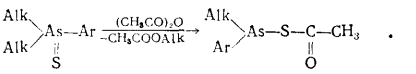


The study of the rearrangement of ethylphenyl-α-naphthylarsine sulphide under the influence of methyl iodide and ethyl bromide established[116] that the arsine sulphide is converted into the ester of the corresponding thioarsinous acid with elimination of the alkyl group. The authors[116] suggest that the reaction pathway can change depending on the reaction conditions. If the reaction is carried out in dry benzene, then the above pathway predominates; however, in the absence of a solvent it proceeds in the opposite direction. Analogous results were obtained[117] in a study of the rearrangement of ethylphenyl-*p*-tolylarsine sulphide.

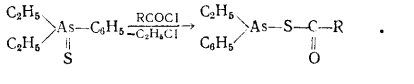
The formation of thioarsinous acids was noted in the rearrangement of diethylphenylarsine sulphide under the influence of carboxylic acids[118]



The rearrangement of dialkylarylarsine sulphides under the influence of carboxylic acid anhydrides[118] leads to the corresponding mixed anhydrides:



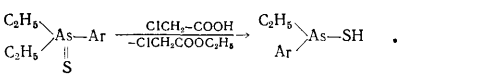
The reaction with carboxylic acid halides takes place similarly[118]:



The ease of reaction depends on the nature of the reactants. Compared with acid anhydrides, the corresponding acid chlorides are more reactive. The reactivity falls with increase in the length of the hydrocarbon chain. For

example, it has not been possible to obtain the products of the isomerisation of diethylphenylarsine sulphide under the influence of palmitoyl chloride.

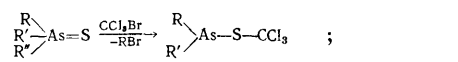
The reaction of diethylphenylarsine sulphide with chloroacetic acids yields the corresponding ethylphenylthioarsinous acids [119,120]:



The rate of reaction increases with increasing number of chlorine atoms in the acid molecule.

It has been shown by differential thermal analysis [121] that the rearrangement [122-124] begins with electrophilic attack by the alkyl group on the sulphur atom. The positive charge, which has arisen on the arsenic atom via an inductive mechanism, polarises the As–C bond, which breaks when attacked by the anion. This results in the formation of the corresponding thioarsinite ester and alkyl halide. The course of the process depends on the nature of the halogen and of the hydrocarbon group.

The analogous reactions of dialkylaryl- and trialkylarsine sulphides with bromotrichloromethane have been described [125]. They lead to the formation of the corresponding trichloromethyl esters of asymmetric thioarsinous acids:

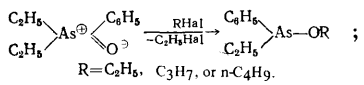


R=CH_3, C_2H_5, C_3H_7, or n-C_4H_9; R′=C_6H_5 .

It is suggested that, under mild conditions (heating of the reactants in benzene or nitromethane), the reaction proceeds via the mechanism described above, involving the electrophilic attack. The interaction of the above sulphides with bromotrichloromethane at 180°C in a sealed tube can evidently proceed also via a radical mechanism [126-128].

An analogous rearrangement is undergone by arsonic acid esters, for which it was first discovered [129] in 1947, and by arsine oxides [130] although it has been stated in a number of studies [131-133] that the rearrangement of oxides is more complex than that of arsine sulphides. However, in both cases the final reaction products are the corresponding esters.

It has been shown [133] that, when diethylphenylarsine oxide reacts with alkyl bromides, the corresponding esters of ethylphenylarsinous acid are formed in 70% yield:



R=C_2H_5, C_3H_7, or n-C_4H_9.

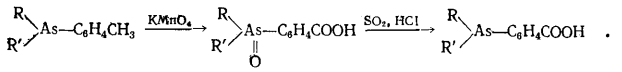
According to the authors [133], the reaction mechanism involves the conversion of diethylphenylarsine oxide into a quasi-arsonium salt, which is then converted further into an ester of ethylphenylarsinous acid with liberation of ethyl halide. The intermediates could not be obtained in a pure form for a long time. The isolation of some of them has been reported only in the latest studies [132,133]. However, the products obtained are extremely unstable under the usual conditions. On exposure to atmospheric moisture, they are converted into oxyarsonium salts with rupture of the O–R bond.

Thus it was shown in the above investigations that the reactions of tertiary arsine sulphides and oxides under the influence of electrophiles take place in the direction opposite to that of the Arbuzov rearrangement [134].

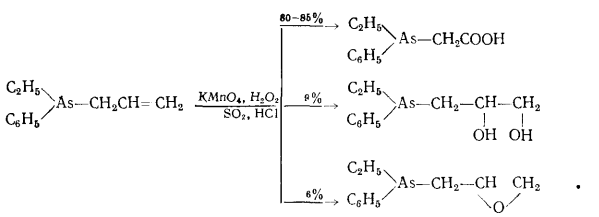
6. Arsines with Functional Groups

Organoarsenic compounds with functional groups, for example arsenic-containing acids or amines, are used in the resolution of racemic arsines with the aid of optically active components.

Asymmetric arsines of the type $RR'AsC_6H_4COOH$ have been synthesised [135-137] by oxidising the corresponding tolylarsines with aqueous $KMnO_4$ and subsequent treatment with gaseous sulphur dioxide in hydrochloric acid:

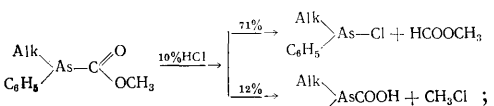


Ethylphenylarsinoacetic acid has been obtained by oxidising allylethylphenylarsine [138] with a solution of $KMnO_4$ and 26% H_2O_2 followed by reduction. This results in the formation of several side products, but ethylphenylarsinoacetic acid is obtained in a high yield:



Racemic ethylphenylarsinoacetic acid was isolated from the mixture of products by repeated vacuum distillation.

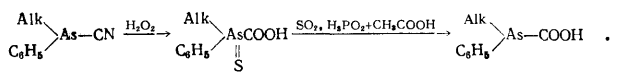
Alkylarylarsinoformic acids have been obtained [139] by hydrolysing the corresponding esters and nitriles and by carbonating sodium arsenides:



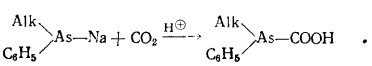
Alk=CH_3, C_2H_5, or n-C_3H_7.

Hydrolysis of methyl ethylphenylarsinoformate with 10% HCl leads to a mixture of products—a halogenoarsine and arsinoformic acid.

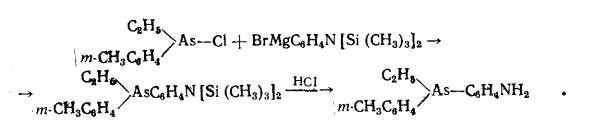
Hydrolysis [110] of arsinonitriles proceeds with formation of arsinoformic acid oxides, which are then reduced by sulphur dioxide to a mixture of hypophosphorus and acetic acids:



When sodium arsenides were carbonated [110], the corresponding arsinoformic acids were obtained in 75% yield:



Asymmetric aminoarsines of the type $RR'AsC_6H_4NH_2$ have been synthesised with the aid of organosodium [140,141] and organomagnesium compounds [142]:



IV. STEREOCHEMISTRY OF ORGANOARSENIC COMPOUNDS

1. Configurational Stability

It was impossible for a long time to obtain stable optically active forms of phosphines and arsines. The difficulty of synthesising optically active phosphorus and arsenic compounds was explained by their low barrier to inversion[143], which apparently occurred via a planar transition state[144].

The inversion frequencies of phosphorus and arsenic hydrides were determined from spectroscopic data[145] (5×10^6 s^{-1} for PH_3, 16×10^4 s^{-1} for AsH_3, 6×10^2 s^{-1} for PD_3, and 30 s^{-1} for AsD_3). Evidently they decrease significantly with increasing mass of the substituents. This shows that the configurational stability should increase on passing to compounds with organic groups. Weston[146] calculated the temperatures at which the racemisation half-life of a number of compounds of Group V elements is 2 h. The temperatures for trimethylphosphine and trimethylarsine are 280° and 380°C respectively and the corresponding energies of the inversion barrier are 22.0 and 29.2 kcal $mole^{-1}$. These values were confirmed also by other workers. It has been shown experimentally[147,148] that, in the racemisation of methyl-n-propylphenylarsine, the inversion barrier reaches 28–30 kcal $mole^{-1}$, which indicates a fairly high configurational stability of tertiary racemisation of methyl-n-propylphenylarsine, the inversion barrier reaches 28–30 kcal $mole^{-1}$, which indicates a fairly high configurational stability of tertiary arsines in non-catalysed thermal racemisation.

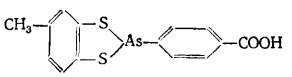
The racemisation of optically active isomers of ethylmethylphenylarsine has been investigated[149] in decalin at 217.6° ± 0.3°C. The activation energy for the inversion of these optical isomers is 42.4 ± 0.5 kcal $mole^{-1}$ at 217.6°C.

It has been shown[150–153] that, on heating at 200°C for 10 h, ethylmethylphenyl- and methylphenyl-n-propylarsines do not lose their optical activity. It has been suggested[150–153] that the calculated racemisation half-life of ethylmethylphenylarsine at 200°C is approximately 740 h. The energy required for the thermal racemisation of the above tertiary arsines should be 59.3–61.0 kcal $mole^{-1}$.

The configurational stability of optically active compounds of Group V elements depends not only on the nature of the central atom but also on the nature of the substituents and the strength of their bonds with the asymmetric atom. For example, it has been shown[154] that, on replacement of one of the three substituents in analogous trisubstitued compounds of nitrogen, phosphorus, and arsenic by groups containing arsenic, phosphorus, silicon, germanium, and tin, the inversion barrier decreases[155].

The configurational stability of arsines and analogous phosphines varies similarly as a function of structure[156] (Table 1). Consequently the electronegativity of the neighbouring heteroatom has a dominant influence on the configurational stability of the above compounds. This is confirmed by the data in Table 1, which show that an increase of the electronegativity of the heteroatom entails an increase of the energy of the barrier. The configurational stability depends also on the $p_\pi - d_\pi$ and $p_\pi - p_\pi$ conjugation of the substituents with the heteroatom[157].

Cyclic compounds of tervalent phosphorus and arsenic exhibit a high configurational stability. The optical activity of these compounds also persists on prolonged heating in non-polar solvents. For example, on heating in chloroform or ethanol, the optical activity of 2-carboxyphenyl-5-methyl-1,3-dithia-2-arsindan (VII) persists, but in an alkaline solution, the compound racemises very rapidly[158].



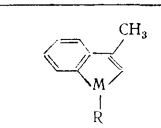
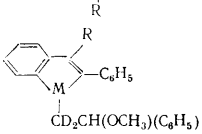
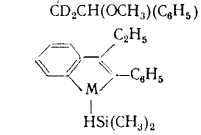
(VII)

According to the authors, the racemisation takes place as a result of the rupture of an As–S bond.

Table 1. Inversion barriers in tertiary arsines and phosphines[156,157].

Compound	Energy of inversion barrier, kcal $mole^{-1}$ (T, °C)	
	E = As	E = P
$(C_6H_5)(CH_3)ER$	43.1 (218)	33.3 (130)
$(C_6H_5)(CH(CH_3)_2)ESi(CH_3)_3$	25.1 (181)	18.9 (62)
$(C_6H_5)(CH(CH_3)_2)EGe(CH_3)_3$	27 (200)	21.4 (109)
$(C_6H_5)(CH(CH_3)_2)ESn(CH_3)_3$	25.9 (191)	19.3 (72)
$(C_6H_5)E(SiH)(CH_3)_2$	17.7 (49)	12.2 (42)

Table 2. Inversion barriers in cyclic arsines and phosphines[159].

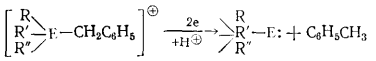
Compound	Energy of inversion barrier, kcal $mole^{-1}$ (T, °C)	
	E = As	E = P
	46.48	35.3 (130)
	35.2 (151)	23.7 (165)
	24.3 (161)	16.6 (180)

The barrier to inversion in certain phospha- and arsaindoles is also lower (Table 2) than for acyclic arsines and phosphines (Table 1).[159] The decrease of the barrier in cyclic compounds probably occurs as a result of the involvement of the free electron pair of phosphorus or arsenic in $(3p_\pi - 2p_\pi)$- or $(4p_\pi - 2p_\pi)$-cyclic delocalisation in the planar transition state.

The configurational stability of optically active phosphines and arsines depends also on the solvent. The probability of the loss of optical properties increases in polar solvents. The process can take place both with complete racemisation and with inversion of configuration.

2. Tertiary Arsines

The positive results obtained in the study of the optical isomerism of cyclic phosphorus and arsenic compounds[160-175] aroused interest in the study of the optical properties or acyclic tertiary phosphines and arsines. Stable enantiomers of the type RR′R″E were not obtained until 1961.[176-179] They were synthesised by the electrochemical reduction of optically active phosphonium and arsonium salts at a mercury cathode.



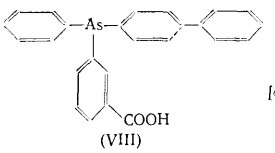
(+) or (−) (+) or (−)

E = P or As

R	R′	R″	$[\alpha]_D^{20}$
CH_3	C_2H_5	C_6H_5	+15.0°
CH_3	C_3H_7	C_6H_5	+16.8°
CH_3	C_2H_5	C_6H_5	+1.9°
CH_3	C_4H_9	C_6H_5	+12.4°

The dextro- and laevo-rotatory isomers of benzyl-n-butylmethylphosphine with the specific rotations $[\alpha]_D^{27} = 24.0°$ and $[\alpha]_D^{27} = -28.2°$ were obtained later[180]. They were synthesised by cleaving with sodium methoxide the optically active (−)- and (+)-isomers of acid benzyl-n-butyl-β-cyanoethylmethylphosphonium dibenzoyltartrates.

The next stage in the development of the stereochemistry of tertiary arsines involved the search for easier methods for the resolution of non-heterocyclic arsines. Asymmetric arsenic derivatives could not be resolved for a long time via their diastereoisomeric salts. The failure was associated with the difficulty of selecting optically active reagents and solvents as well as the appropriate conditions for the fractional crystallisation of diastereoisomeric pairs. An acyclic tervalent arsenic compound (VIII) was resolved only recently using this classical method[181]:



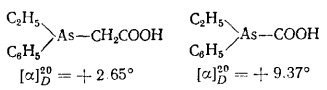
(VIII)

$[\alpha]_D^{20} = +8°$, $[\alpha]_D^{20} = -7°$.

The resolution of triaryl- and alkyldiaryl-arsines containing a functional group (COOH, NH_2) in the aromatic ring has been reported in a number of studies[135-137,182]. (+)-Quinine, (−)-α-phenylethylamine, morphine, and (+)-tartaric acid were used respectively as the asymmetric reagents for the separation of these compounds into optically active isomers. The diastereoisomeric salts were decomposed by treatment with an excess of H_2SO_4 and NH_4OH solutions. The specific rotations of the enantiomers were determined in benzene.

R	R′	R″	$[\alpha]_D^{20}$ (+)	$[\alpha]_D^{20}$ (−)
C_2H_5	$C_{10}H_7$-β	C_6H_4COOH-*o*	6.04°	4.94°
C_2H_5	C_6H_5	C_6H_4COOH-*n*	11.64°	5.35°
C_2H_5	C_3H_7-*n*	C_6H_4COOH-*n*	3.01°	2.12°
C_2H_5	$C_6H_4CH_3$-*o*	$C_6H_4NH_2$-*o*	2.69°	2.34°

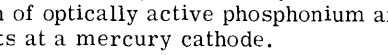
Ethylphenylarsinoacetic[138] and arsinoformic[183] acids were resolved similarly with the aid of (−)-α-phenylethylamine and quinine.



$[\alpha]_D^{20} = +2.65°$ $[\alpha]_D^{20} = +9.37°$

3. Tetracoordinate Compounds

The study of the optical properties of phosphonium[184-187] and arsonium[188-190] salts showed that most of them lose their optical rotation in polar solvents (acetone, alcohol), possibly owing to dissociation to the initial phosphines or arsines and the corresponding alkyl halides:

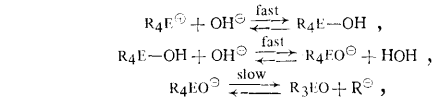


R=CH_3; R′=C_2H_5, R″=C_6H_5; R‴=$C_6H_5CH_2$; Hal=Cl, Br, or I; E = P or As.

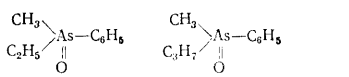
Depending on the nature of the halogen, the rate of racemisation[191] increases in the sequence Cl < Br < I.

The results of the study of the relative configurations of phosphonium and arsonium salts are also of much interest. When optically active tertiary arsines react with alkyl halides, optically active arsonium salts with the same sign of rotation as in the initial arsines are obtained. However, the absolute value of the specific rotation of the salts is greater than that of the initial arsines. This confirms that the hydrocarbon group adds to the arsenic atom via the free electron pair with retention of its relative configuration.

In an alkaline medium optically active phosphonium and arsonium salts are converted into the corresponding oxides[192]. The stereospecific resolution of these salts consists of several stages whose stereochemical mechanism has been examined in detail[193-195]:



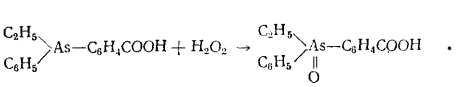
New ways of synthesising optically active tertiary phosphine oxides by the direct oxidation of the corresponding enantiomers have now become available[176]. However, it was for a long time impossible to obtain optically active arsenic oxides with the aid of this method. Horner and Winkler[196] reported the synthesis and a study of the enantiomers of ethylmethyl- and methyl-n-propylphenyl-arsine oxides:



$[\alpha]_D^{20} = +2.4°$ $[\alpha]_D^{20} = +6.4°$; $-18.0°$

It was found that these oxides are optically unstable and racemise rapidly. Evidently the conversion of the oxides into the racemic modification is achieved by their conversion into the hydroxide under the influence of moisture.

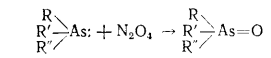
An attempt to obtain optically active tertiary arsine oxides by oxidising the enantiomers of aliphatic-aromatic arsines by H_2O_2 under mild conditions has been reported[197]:



However, the products obtained in this reaction did not exhibit an optical activity.

Owing to the extremely high hygroscopicity of the above oxides, they were synthesised[198] by oxidising optically active tertiary arsines with nitrogen dioxide in dry

nitromethane.

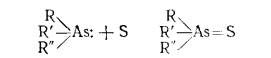


R	R′	R″	$[\alpha]_D^{20}$ (+)	$[\alpha]_D^{20}$ (−)
C_2H_5	C_3H_7-n	C_6H_4COOH-p	8.63°	7.54°
CH_3	C_6H_5	C_6H_4COOH-p	11.84°	9.26°
C_2H_5	C_6H_5	C_6H_4COOH-p	13.52°	10.92°
C_2H_5	C_6H_5	C_6H_4COOH-o	21.28°	23.59°

The racemisation of the oxides was studied by differential thermal analysis [193,199]. The formation of hydroxides was confirmed on the basis of the differential thermographic curves obtained in the course of the oxidation of (+)-p-carboxyphenylethylphenylarsine and the decrease of the specific rotation.

In contrast to their phosphorus analogues, the enantiomers of arsine oxides are optically unstable and show a tendency towards racemisation regardless of the methods and conditions of their synthesis. The rate of racemisation also depends on solvents, increasing in the sequence benzene < chloroform < nitromethane.

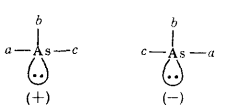
Compared with the oxides, arsenic sulphides are stable. They have been investigated by a number of workers [177,200,201], who were able to resolve them into opically active isomers via diastereoisomeric salts. A convenient method for the synthesis of sulphides, consisting in the interaction of the corresponding arsine with elemental sulphur, has been proposed by Horner and Fuchs [177]. Using this procedure, they obtained from (+)-ethylmethylphenylarsine the enantiomer of its sulphide with the same sign of rotation. Both racemic forms [202] of asymmetric arsenic sulphides [the attempt to separate them chromatographically [203] with the aid of (+)-lactose, (+)-glucose, (+)-starch, and (+)-quartz was unsuccessful] and optically active sulphides [204,205] have been obtained by this procedure.



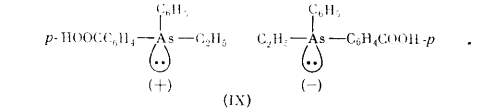
R	R′	R″	$[\alpha]_D^{20}$ (+)	$[\alpha]_D^{20}$ (−)
C_2H_5	C_3H_7-n	C_6H_4COOH-p	3.84°	4.02°
C_2H_5	C_4H_9-n	C_6H_4COOH-p	7.32°	7.73°
CH_3	C_6H_5	C_6H_4COOH-p	12.50°	9.31°
C_2H_5	C_6H_5	C_6H_4COOH-p	19.23°	16.93°

It has been shown that the addition of sulphur to arsenic takes place with retention of the sign of the rotation of the initial enantiomer. It has been established that, when the compounds obtained are heated in benzene at up to 100°C, racemisation does not occur. However, at higher temperatures slow racemisation is observed. It is probably caused by the fact that at high temperatures the enantiomers of the sulphides isomerise to the corresponding thioesters [206].

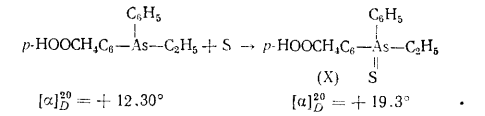
It has been suggested [207] that the (+)-enantiomer has a configuration in which the substituents are arranged in order of their decreasing polarisability in the sequence $a > b > c$. The arrangement of substituents in the opposite sequence corresponds to the (−)-enantiomer.



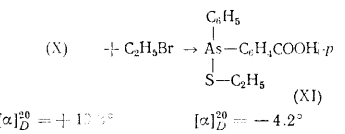
According to this scheme, the molecules of (+)- and (−)-enantiomers of p-carboxyphenylethylphenylarsine (IX) have the following form:



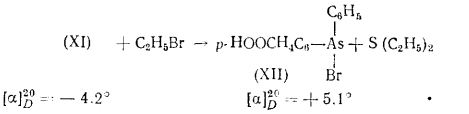
The relative configuration of (IX) has been studied [207] with the aid of the reaction of the (+)-enantiomer with sulphur:



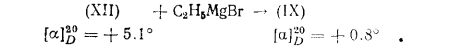
The formation of the (+)-enantiomer of the sulphide (X) with a high specific rotation is due to the increase of the asymmetry of the entire molecule, since the reaction takes place with retention of the relative configuration of the initial product. The interaction of (+)-(X) with ethyl bromide leads to the formation of a product with the opposite sign of rotation [204]. The explanation is that the reaction proceeds via a bimolecular mechanism, involving the bonds between the asymmetric arsenic atom and two substituents. The substituents are arranged during the reaction in a sequence which is different from that obtaining before the reaction. This is accompanied by the inversion of the configuration and a change in the sign of rotation.



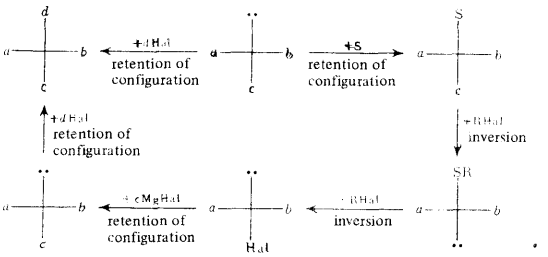
On treatment with ethyl bromide, (−)-(XI) undergoes a further transformation, which leads to the formation of dextrorotatory phenyl-p-carboxyphenylbromoarsine (XII) [207]:



(XII) reacts with ethylmagnesium bromide to form compound (IX) with the same sign of rotation:

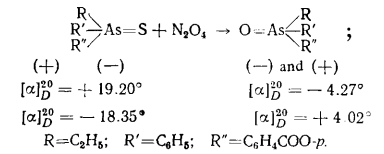


The above cycle of transformations takes place in accordance with the following scheme:

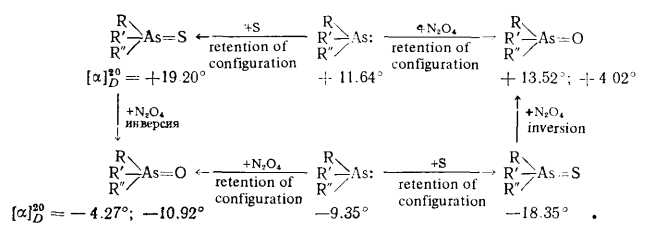


The reaction of optically active sulphides with N_2O_4 [198] in nitromethane at −15°C leads to the formation of the

corresponding oxides with the opposite sign of rotation:

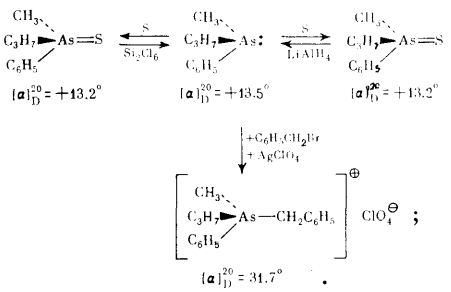


This reaction is accompanied by an inversion of configuration, which follows from the data below:

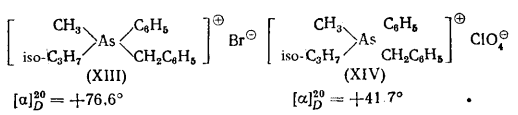


The optically active oxides of acyclic phosphines are reduced stereospecifically by hexachlorodisilane to the corresponding phosphines with inversion of configuration [208]. The reduction of methylphenyl-n-propylarsine sulphide, which has the *R* configuration, with hexachlorodisilane and lithium tetrahydroaluminate proceeds with almost complete retention of configuration at the arsenic atom [209]. The above transformations have been achieved under mild conditions in tetrahydrofuran and di-n-butyl ether.

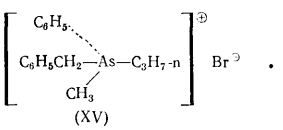
The stereospecific transformations of the arsenic compounds under consideration are illustrated schematically below:



The absolute configuration of chiral isopropylmethylphenylarsonium salts has been determined by the method of quasi-racemates [210]. These salts have been obtained by the reaction of the corresponding diastereoisomers of acid D-(−)- and L-(+)-arsonium dibenzoyltartrates with ammonium bromide and perchlorate in methanol. This led to the isolation of dextro- and laevo-rotatory benzylisopropylmethylphenylarsonium bromide (XIII) and the dextro-rotatory perchlorate (XIV):



The dextro-rotatory benzylmethylphenyl-n-propylarsonium bromide (XV) has the *S*-configuration [211]:



However, when the n-propyl group is replaced by the isopropyl group, the molecular configuration may be inverted [210]. The fusion diagram (Fig. 1) for mixtures of enantiomers of benzylmethylphenyl-n-propylarsonium bromide (XV) with $[\alpha]_D^{20} = +33.4°$ and $[\alpha]_D^{20} = -33.0°$ shows that the enantiomers have a melting point of 188°C, while the racemate melts at 170°C; the eutectic composition is 31% of the (+)-isomer and 69% of the (−)-isomer of compound (XV).

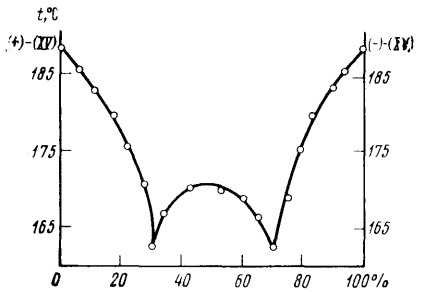


Figure 1. Fusion diagram for a mixture of enantiomers of benzylmethylphenyl-n-propylarsonium bromide (XV).

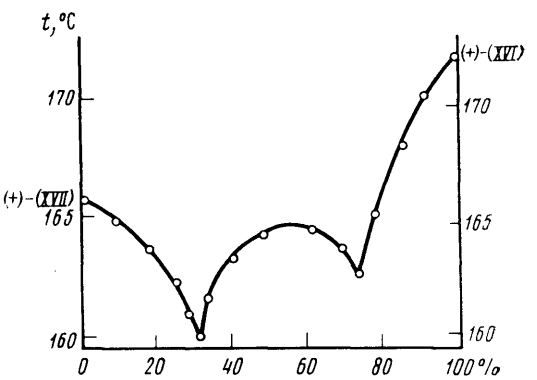


Figure 2. Fusion diagram for a mixture of (+)-(XVI) and (+)-(XVII) tetraphenylborates.

Dextro- and laevo-rotatory benzylmethylphenyl-n-propylarsonium tetraphenylborates (XVI) melt at 172°C, while (+)-benzylisopropylmethylphenylarsonium tetraphenylborate (XVII) has a melting point of 166°C. The fusion diagram (Fig. 2), obtained by combining (XVI) and (XVII) in various proportions, is characteristic of a quasi-racemate with two eutectics melting at 160° and

163°C. This phenomenon shows that the mixture components have the opposite configurations. The same conclusions can be arrived at by comparison with the fusion diagram (Fig. 3) of mixtures of the (+)- and (−)-tetraphenylborates (XVI) in various proportions.

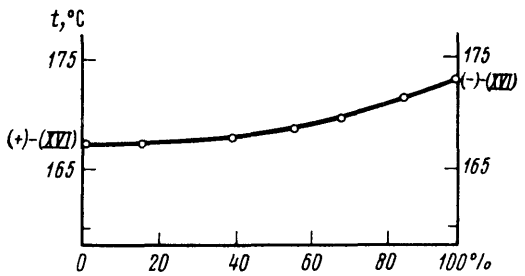
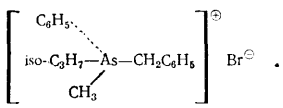


Figure 3. Fusion diagram for a mixture of (+)- and (−)-(XVI) tetraphenylborates.

The above arguments lead to the conclusion that benzylisopropylmethylphenylarsonium (XIII) has the *R*-configuration:



4. The Influence of Substituents in the Benzene Ring on the Optical Activity

It is of definite interest to establish a relation between the structure and the optical rotation of the molecule, which can be followed by introducing various substituents into the aromatic ring joined to the asymmetric atom.

The data in Table 3 show that the absolute specific rotations of *o*-, *m*-, and *p*-carboxy-, methoxycarbonyl-, bromo-, and amino-substituted arylarsines and their sulphides decrease steadily [212-217], although the change is sometimes very slight. When the optical rotations of carboxy-derivatives of arsines and their methyl esters are compared, the specific rotation of the latter is found to be higher than that of the initial arsines. This is probably associated with the increase of the asymmetry of the molecule due to the bulky ester group. The optical rotation of the sulphide is higher than that of the initial arsine enantiomers. This can also be attributed to the increase of the asymmetry of the molecule.

Presumably the change in the optical activities of the above compounds occurs in consequence of the steric influence [218,219] of the substituents on the internal rotation of the groups linked to the asymmetric arsenic atom. The process is evidently accompanied by a change in the "normal" angle of rotation of the aromatic rings. This hypothesis arose when Stuart–Briegleb models were examined. The close proximity of the carboxy-group to the arsenic atom in *ortho*-isomers retards the internal rotation of the groups about the As–C bond axis, which reduces the possibility of the rotation of the phenyl groups and can increase the optical activity of the molecule. In the *meta*-substituted compound the carboxy-group is quite remote from the asymmetric As atom, so that its influence on the attainment of a hindered conformation and the optical activity is diminished. On the other hand, the steric effects due to the presence of two phenyl groups remain, although free rotation remains possible for the ethyl group. In the molecule of the *para*-substituted compound the influence of the carboxy-group on the optical activity is reduced to a minimum, which has been confirmed by the specific rotation.

Table 3. Specific rotations of chiral arsenic compounds of the type $XC_6H_4(C_2H_5)AsC_6H_4Y$. [212-219]
‖
Z

X	Y	Z	$[\alpha]_D^{20}$, °	X	Y	Z	$[\alpha]_D^{20}$, °
H	*o*-COOH	LEP*	+18.36; −18.45	H	*o*-COOH	S	+25.21; −24.81
H	*m*-COOH	LEP	+16.63; −16.41	H	*m*-COOH	S	+23.75; −23.08
H	*p*-COOH	LEP	+12.75; −11.86	H	*p*-COOH	S	+22.56; −21.98
H	*o*-$COOCH_3$	LEP	+25.27; −25.34	*o*-Br	*p*-COOH	S	+23.43; −23.12
H	*m*-$COOCH_3$	LEP	+22.61; −22.30	*m*-Br	*p*-COOH	S	+22.50; −21.88
H	*p*-$COOCH_3$	LEP	+17.44; −17.20	*p*-Br	*p*-COOH	S	+20.40; −19.33
o-Br	*p*-COOH	LEP	+16.80; −16.20	*p*-CH_3	*o*-NH_2	S	+2.81; −2.78
m-Br	*p*-COOH	LEP	+15.20; −14.91	*p*-CH_3	*m*-NH_2	S	+2.49; −2.40
p-Br	*p*-COOH	LEP	+13.54; −13.10	*p*-CH_3	*p*-NH_2	S	+2.23; −1.94
o-CH_3	*o*-NH_2	LEP	+2.69; −2.34	—	—	—	—
o-CH_3	*m*-NH_2	LEP	+2.46; −2.03	—	—	—	—
o-CH_3	*p*-NH_2	LEP	+2.24; −1.72	—	—	—	—

*LEP = lone electron pair.

Table 4. Parameters of the molecular motions of certain tervalent arsenic compounds of the type $RR'AsC_6H_4R''$ according to NMR data [220].

R	R'	Mobile group	T(°C) corresponding to T_1^{min}	T_1^{min}, μs	$T_{1\rho}$, s	Activation energy for reorientation, kcal mole^{-1}
Cl	Cl	H	−29	85	—	—
Cl	Cl	CH_3-*m*	−23	58	—	—
Cl	Cl	OCH_3-*o*	−85	54	$4.2\cdot10^{-13}$	3.35
C_2H_5	Cl	CH_3-*p*	−23	52	$5.6\cdot10^{-15}$	4.6
C_2H_5	Cl	OCH_3-*p*	−105	120	—	—
			−27	52	—	—
			−83	84	$4.2\cdot10^{-13}$	3.35
C_2H_5	C_6H_5	CH_3, CH_3, N	−103	79	$5.6\cdot10^{-15}$	4.6
			−46	43	—	—
			−83	78	$5.6\cdot10^{-15}$	4.6
			−134	82	—	—

The possibility of the rotation of the phenyl group about the As–C bond has been studied [220] by NMR. The specimens used were compounds of tervalent arsenic of the type RR'AsCl and RR'R''As (Table 4), where R = C_6H_5, *p*- and *m*-$CH_3C_6H_4$, or *p*- and *o*-$CH_3OC_6H_4$, R' = C_2H_5, and R'' = $N(CH_3)_2$, for which the spin–lattice relaxation times T_1 and $T_{1\rho}$ were measured. The second moments of the NMR line were calculated by analysing the solid-echo signals. The measurements were made on an NMR pulse spectrometer at a frequency of 27.5 MHz in the temperature range from −190°C to +20°C.

Several relaxation regions, associated with individual forms of intramolecular motion, were observed for all the test specimens. All the arsines containing the ethyl group give rise to a minimum at $10^3 T^{-1} = 6$ on the curve relating the relaxation time to temperature, while for specimens without this group there is no such minimum. This makes it possible to assign the given relaxation region to reorientations of the ethyl group about the As–C bond. Substances containing the methoxy-group exhibit a minimum at $10^3 T^{-1} = 5.5$, which is associated with the mobility of the methoxy-group. The compound containing the dimethylamino-group has a relaxation region at $10^3 T^{-1} = 5.5$ associated with its rotation. At higher temperatures all the specimens exhibit a relaxation period T_1 associated with the mobility of the molecule as a whole. At the temperatures investigated the relaxation regions associated with the mobility of the benzene ring were not observed. The absence of a minimum on the curves for the temperature variation of T_1 and $T_{1\rho}$, corresponding to compounds with a phenyl group, may indicate a greater degree of retardation of the rotation of the aromatic rings. Consequently one can postulate that steric factors hinder the reorientation of the aromatic groups and determine their angle of rotation. This can be in turn one of the causes which determine the angle of rotation of optically active compounds.

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