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Investigations on the Arbuzov and retro-Arbuzov reactions among the organic derivatives of arsenic

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ABSTRACT. Results of attempts to effect the Arbuzov and retro-Arbuzov reactions with esters of arsinous acid and with oxides and sulphides of tertiary arsines have been correlated. The general rules and special features of these conversions are considered as well as the reactions accompanying them as a function of the environment of the arsenic atom, the nature of the electrophilic reagent and the reaction conditions. Recent and previously known results are considered from a common position.

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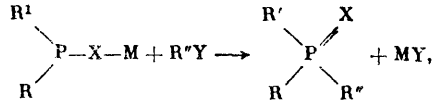
I. Introduction

The problem of nucleophilic reactivity and its link with the nature of the nucleophilic centre, with the character of its surroundings and the degree of coordination is one of the most important and pressing problems of modern chemistry. Investigation of the basic rules and, more specifically, the reactions of organoarsenic nucleophiles with electrophilic reagents is also of particular interest in connection with attempts to effect conversions analogous to the Arbuzov reaction, known in phosphorus chemistry, with the organic derivatives of arsenic. The process occurring in the reverse direction and known as the retro-Arbuzov reaction is also of interest, and has proved to be more characteristic of compounds of tetracoordinated arsenic.[1]

Numerous data have been accumulated to date by domestic investigators.[1–12] However, until now separate, sometimes contradictory, aspects of this problem have been considered which hinder an understanding of the results obtained. These problems are analysed in the present review from a common position in the light of the work of recent years.

II. Attempts to effect the Arbuzov reaction with esters of As(III) acids

After the discovery by A E Arbuzov of the reaction, which has become one of the most important synthetic methods in the chemistry of organophosphorus compounds,[13] numerous attempts were undertaken to effect a similar conversion among the organic compounds of arsenic, the closest analogue of phosphorus. On the one hand these attempts were justified by the importance acquired by the Arbuzov reaction in phosphorus chemistry. On the other hand, there is some basis to suppose that a similar reaction with the esters of trivalent arsenic is, in principle, possible. There is, in fact, the well known Michaelis–Becker reaction in the chemistry of arsenic.[14]



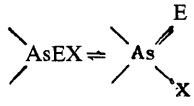
R, R′=Alk, Ar, AlkO; R″=Alk, Ac;
X=O, Y=Hal; M=metal

This reaction may correspond to one of the most important reactions in the arsenal of synthetic methods for this element, viz. the Meyer reaction and its modification proposed by Ozhe,† Scheller, Bart and others.[14]

$$Na_3AsO_3+RHal\rightarrow RAs(O)(ONa)_2+NaHal,$$
$$RAs(ONa)_2+R'Hal\rightarrow RR'As(O)ONa+NaHal,$$
$$R_2AsOAsR_2+2RI\rightarrow 2R_3AsO+2NaI,$$
$$RAs(ONa)_2+ArN_2Hal\rightarrow RArAs(O)ONa+N_2+NaHal,$$
R, R′=Alk; Hal=Cl, Br, I.

The point of this process, as for phosphorus derivatives, is an increase in the degree of coordination of the central atom, which is accompanied by the appearance of a new C–E bond and the generation of an E(O) grouping, where E = P, As. The conditions for carrying out these reactions are also closely similar.

Judging by the analogous phosphorus derivatives, the problem of tautomerism will arise in the arsenic compounds.



, where X=H, M.

However this problem has not been studied in practice. For phosphorus compounds, as is known,[15] the tautomeric equilibrium lies markedly to the right.

† This name is a transliteration and may be in error (Ed. of Translation).

Unlike phosphorus acid, arsenous acid is tribasic. Its triply substituted salts are well known. This suggests that the equilibrium of the tautomeric conversion, if it occurs among trivalent arsenic derivatives, is shifted in the direction of compounds with a lower degree of coordination of the central atom.

The need to use an alkaline medium, in spite of a whole range of side reactions, is a general feature of the conversions under examination. This is evidently linked with the high stability of tetracoordinated derivatives of arsenic in alkaline medium.

At the same time, as is well known,[16] the stability of the highest valence state of the IVth period *p* elements, as in other subgroups of the Mendeleev periodic system, is significantly less than in the IIIrd period. Consequently it might be expected that conversions accompanied by an increase in the degree of coordination must be less characteristic for arsenic derivatives than for the phosphorus analogues.

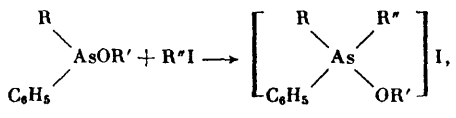
In reality, attempts to isomerise esters of As(III) acids, carried out under the conditions of the Arbuzov reaction, gave negative results. No isomerisation was observed on heating equimolar quantities of alkyl esters of phenyl- and diphenylarsinous acids with methyl and ethyl iodide for a fairly extended time (up to 18 h) at temperatures of 100–102 °C.[2]

Similar attempts were made with practically all possible classes of esters of trivalent arsenic acids, including fully esterified arsenous acid $(RO)_3As$ where R = Alk or Ar, alkyl and aryl esters of alkylarsonous acids $RAs(OR)_2$ and esters of dialkyl- and alkylphenylarsinous acids RR′AsOr″.[2]

In no case was isomerisation successfully recorded in spite of varying the reaction conditions and the reactant ratios.

Several authors have recorded cases when crystalline products were formed on reacting esters of trivalent arsenic acids with alkyl halides. Kamai and collaborators[2] first paid attention to this phenomenon but the structure of the products remained unclarified. The reaction of the triethoxypropyleneglycol ester of ethylarsinous acid with methyl iodide was also recorded and leads to the formation of a crystalline product close in composition to a trimethylethylarsonium salt.[2]

Later[17] crystalline products were isolated on reacting alkyl esters of alkylphenylarsinous acids with alkyl halides, which were assigned the structure of dialkylphenylalkoxyarsonium salts on the basis of data of arsenic and halogen analysis. The authors assumed that the reaction proceeds in a manner similar to the first stage of the Arbuzov rearrangement.



R, R′, R″=CH_3, C_2H_5, C_3H_7, C_4H_9.

Following this, communications appeared on the isolation of trialkylalkoxyaronsium salts from the reaction of esters of dialkylarsinous acids with alkyl halides.[2] The authors also used only data of elemental analysis for arsenic and halogen to infer the structure of the products formed.

Thus for esters of trivalent arsenic containing only one alkoxy group, the reaction is similar to the Arbuzov rearrangement as though stopped at the first stage.

Attention is also drawn to the fact that some properties of the products of the reaction of esters of dialkyl- and alkylphenylarsinous acids with alkyl halides do not correspond completely with the properties of alkoxy-arsonium salts. Thus dialkylphenylalkoxyarsonium iodides exchange iodide ion for nitrate ion on heating with dilute nitric acid with no change in the composition of the cation containing the alkoxy group.[2] However it is well known that an alkoxy group on an arsenic atom is fairly sensitive to hydrolysis.

The inconsistencies indicated call for a wider investigation of the products which were assigned the structure of alkoxyarsonium salts. Such investigations were subsequently undertaken.[6] The result was the unexpected conclusion that alkoxy groups were not present in the crystalline products examined. Data of IR and PMR spectra, results of conductiometry, comparison of physicochemical characteristics and data of more complete elemental analysis of the reaction products indicated that alkoxyarsonium salts were not formed by the reaction but the products were the well known quaternary arsonium salts containing no alkoxy groups.

$$RR'AsOR''+RX\rightarrow[R_3R'As]X.$$

Evidently the lack of using spectroscopic methods, the small difference in elemental composition for the compounds $[R'R_2AsOAlk]X$ and $[R'R_2AsAlk]X$, which are close in structure, and also the suggestive analogy with the first stage of the Arbuzov rearrangement biased the authors, working in this area for the first time, towards that structure for the products which seemed to be expected naturally in the reactions examined.

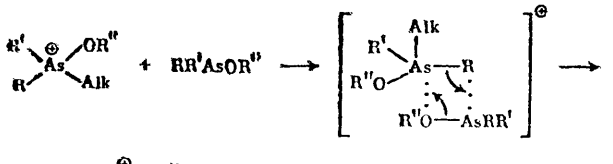
Subsequent investigations of this reaction carried out on several series of esters of dialkyl- and alkylphenylarsinous acids,[18] showed that the composition of the quaternary arsonium salts formed did not depend on the nature of the hydrocarbon residue in the ester group. This enabled exclusion of the scheme proposing exchange of hydrocarbon residues between the alkoxy group of the ester and the alkyl halide from the number of possible reaction schemes.

$$RR'AsOR''+RX\not\rightarrow RR'AsOR+R''X$$

Of the possible schemes proposed to explain the formation of quaternary arsonium salts in this reaction, two are most probable. According to one of them (Scheme 1) the increase in the coordination number of the arsenic atom occurs at the first stage.[6,9]

Scheme 1

$$RR'AsOR''+AlkHal\rightarrow[RR'AlkAsOR'']^{\oplus}Hal^{\ominus}, \quad (1)$$



$$\rightarrow R'Alk\overset{\oplus}{As}(OR'')_2 + R_2R'As, \quad (2)$$

$$R_2R'As+AlkHal\rightarrow[R_2R'AlkAs]Hal. \quad (3)$$

The alkoxyarsonium cation formed, being unstable to nucleophilic attack, is converted into the corresponding tertiary arsine by the action of a second molecule of the initial ester [Scheme 1, stage (2)]. The appearance of a tertiary arsine in the presence of the alkyl halide leads to the formation of the quaternary arsonium salts [Scheme 1, stage (3)].

Another possible reaction route (Scheme 2) consists of a disproportionation of the initial ester, which also leads to the appearance of tertiary arsines, and as a result to the isolation of quaternary arsonium salts as final products [Scheme 1, stage (3)].[6]

Scheme 2

$$2RR'AsOR'' \rightleftharpoons R_2R'As + R'As(OR'')_2.$$

As the reaction mechanism was unexplained, an invetigation of its kinetics was later undertaken.[19] Partial reaction orders, determined by a differential method, for the case of the ethyl ester of diethylarsinous acid and ethyl iodide in acetone at 50 °C proved to be close to unity, which indicates an overall second order. The comparatively simple kinetics for a reaction which is evidently not so simple are explained by the authors by the presence of a limiting step, most probably at the beginning of the process.

It became clear later that the method of obtaining the initial ethyl ester of diethylarsinous acid has an effect on the kinetic data.

$$(C_2H_5)_2AsCl + NaOC_2H_5 \rightarrow (C_2H_5)_2AsOC_2H_5 + NaCl.$$

Haloarsine and tertiary arsine contaminants contained in the reaction product distort the kinetics of the process in the case of the simpler and therefore more frequently used method.

On making the initial ester from bis(diethylarsine)oxide the data of the kinetic investigation proved to be more stable and led to a reproducible result.[9,19]

$$[(C_2H_5)_2As]_2O + 2C_2H_5OH \xrightarrow[-H_2O]{} 2(C_2H_5)_2AsOC_2H_5.$$

It should be noted that both routes considered as most probable for forming quaternary arsonium salts propose the appearance in the reaction mixture of the same products, viz. esters of arsonous acids $R'As(OR'')_2$. These esters were successfully isolated somewhat later.[20]

$$2RR'AsOR'' + AlkX \rightarrow [R_2R'AsAlk]X + R'As(OR'')_2,$$

Alk=R=R'=C_2H_5, R''=C_6H_5, X=I;

Alk=R=C_2H_5, R'=C_6H_5, R''=C_4H_9, X=I;

R=R'=C_2H_5; R''=Alk=C_4H_9, X=Br.

It is interesting that the possibility of forming quaternary arsonium salts by a similar reaction was also discovered for esters of arsonous acids.[9]

$$3C_2H_5As(OC_2H_5)_2 + C_2H_5I \rightarrow [(C_2H_5)_4As]I + 2(C_2H_5O)_3As.$$

Further investigations showed that in the case of the lower esters of dialkylarsinous acids the formation of alkoxyarsonium salts may nevertheless be observed under fairly mild conditions.[21]

$$(CH_3)_2AsOCH_3 + CH_3I \rightarrow [(CH_3)_3AsOCH_3]I.$$

The structure of the product was confirmed by IR and PMR spectroscopy. However in addition to bands (655, 1013 cm^{-1}) indicating the presence of the $\rangle AsOC\langle$ grouping, signs of hydroxyl were detected which the authors link with admixture of a compound arising as a result of hydrolysis.

$$[(CH_3)_3AsOCH_3]I + H_2O \rightarrow [(CH_3)_3AsOH]I + CH_3OH.$$

The formation of hydroxyarsonium salts in the reaction of the ethyl ester of dicyclohexylarsinous acid with ethyl iodide is also linked with the increased sensitivity of alkoxyarsonium salts towards hydrolysis.[9]

Cases of the formation of difficultly separable mixtures containing, in the authors' opinion, alkoxyarsonium salts were also noted in the case of the ethyl ester of diethylarsinous acid. However, another product is proposed as contaminant here, viz. a quaternary arsonium salt containing no alkoxy group.[20]

$$(C_2H_5)_2AsOC_2H_5 + C_2H_5I \rightarrow [(C_2H_5)_3AsOC_2H_5]I + [(C_2H_5)_4As]I.$$

On the basis of this the hypothesis was made that tetraethylarsonium iodide is formed from the corresponding alkoxyarsonium salt, i.e. Scheme 1 (see above). However such an interpretation is seemingly not indisputable since the combined isolation of two products does not always indicate that one is not formed from the other. The most persuasive confirmation of the scheme in question might be to attempt to convert the alkoxyarsonium salt directly into a quaternary arsonium salt. So far this has not been successful.

Scheme 2, proposing the disproportionation of the intial ester, is less vulnerable. This property of the esters of As(III) acids was confirmed by GLC.[22] The results obtained by chromatography indicate that the disproportionation is essentially an important property of esters of arsinous acids, which it is impossible not to consider when analysing conversions involving them. The presence in the reaction mixture of haloalkanes capable of binding the generated tertiary arsine in the quaternary arsonium salt isolated in the solid may be considered as a factor assisting disproportionation.

At the same time it would be premature to make a final conclusion regarding the route of formation of the quaternary arsonium salts in the reaction.

Attempts have also been undertaken to effect conversions like the Arbuzov reaction in several thioesters of trivalent arsenic acids. However they were also unsuccessful here. The appearance of another nucleophilic centre, the sulphur atom, together with the arsenic atom evidently leads to a change in the direction of attack of the nucleophile and the reaction leads to the formation of dialkyl disulphides or sulphonium salts.[8,23]

$$R_nAs(SR')_{3-n} + (3-n)R''X \longrightarrow$$

$$\longrightarrow [R_nAs(SR')^{\oplus}_{2-n}SR'R'']X^{\ominus} \longrightarrow R_nAsX_{3-n} + (3-n)R'SR'',$$

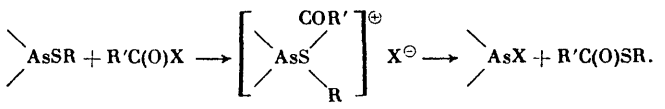
R=C_2H_5, C_6H_5, $NH(C_6H_4)_2$; R'=C_2H_5, C_4H_9,



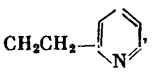
—CH_2CH_2, $C(O)CH_3$, CH_2CH_2OH, $C_6H_4NH_2$-o;

R''=CH_3, C_2H_5; X=Br, I; n=0, 1, 2.

Similarly carboxylic acid chlorides react with thioesters with fission of the As–S bond.[5] Reaction occurs at the sulphur atom as in the case of the alkyl halides.

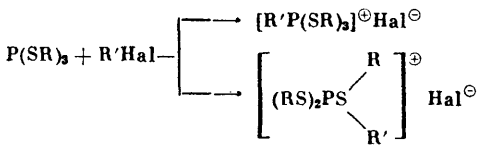


$$R=C_4H_9,\ CH_2CH_2OH,\ CH_2CH_2N(C_2H_5)_2,$$



$$R'=CH_3,\ C_6H_5;\ X=Cl,\ Br.$$

Such a reaction course is not unexpected since even thiophosphites, in which the phosphorus atom is more nucleophilic than arsenic in the thioesters of the corresponding As(III) acids, may be alkylated under analogous conditions both at phosphorus and at sulphur.[24–33]



It is interesting to compare these data with the conversions of antimonous acid under the action of halogen derivatives.[34]

$$Sb(OR)_3+nR'X\rightarrow X_nSb(OR)_{3-n}+nROR'$$

$$R=Alk,\ R'=Alk,\ Ac,\ CH_2OAlk;\ X=Cl,\ Br,\quad n=1\text{ to }3.$$

The formation of an oxonium compound was proposed at an intermediate stage and the process itself is considered as a variation of the Williamson reaction, i.e. the reaction of alkyl halides with alkoxides. In the opinion of the author, the polarity of the E–O bond changed in derivatives of the type $(RO)_3E$ (E = P, As, Sb). The phosphorus atoms acts as the nucleophilic centre in phosphites (E = P) and the oxygen atom in esters of antimonous acid (E = Sb). A similar approach was also confirmed by the results of other conversions.[34]

$$(RS)_3Sb+nR'X\rightarrow (RS)_nSbX_{3-n}+(3-n)RSR',$$
$$R=Alk;\ R'=Alk,\ Ac;\ X=Cl,\ Br,\ I,$$
$$(C_2H_5O)_3P+3HBr\rightarrow H_3PO_3+C_2H_5Br,$$
$$(C_2H_5O)_3As+3HBr\rightarrow AsBr_3+3C_2H_5OH.$$

Returning to the esters of arsinous acids it is interesting to note the attempt to alkylate their anhydrides $(RR'As)_2E$ (E = O, S),[35] which may be considered as derivatives of esters RR'AsER'' when R'' = AsRR'. It is assumed that the presence of a system of three interconnected nucleophilic centres may change the ratio of their nucleophilicities and make the first stage of the Arbuzov reaction more probable.

As it turned out, in this case also the reaction occurs in a more complex manner and led to the formation of a quaternary arsonium salt and haloarsines. When using thioanhydrides the reaction requires more forcing conditions and is accompanied by side reactions.

$$RR'AsEAsRR'+RX\rightarrow RR'AsER+RR'AsX,$$

when E = O [Ref. 35]:

$$RR'AsOR+RX\rightarrow [R_3R'As]X,$$
$$RR'AsX+RX\rightarrow R_2R'AsX_2,$$

when E = S [Ref. 36]:

$$RR'AsSR+RX\rightarrow RR'AsX+[R_3R'As]X,$$
$$R=R'=C_2H_5,\ n\text{-}C_3H_7,\ iso\text{-}C_3H_7,\ n\text{-}C_4H_9,$$
$$R=Alk,\ R'=C_6H_5;\ X=Br,\ I.$$

In similar reactions the corresponding esters and haloarsines were isolated from acid chlorides of carboxylic acids.[35]

$$(RR'As)_2E+R''X\rightarrow RR'AsER''+RR'AsX,$$
$$R=R'=Alk,\ C_6H_5;\ R''=CH_3C(O),\ C_6H_5C(O);\ X=Cl.$$

The data presented permit the conclusion that even in the most nucleophilic esters of As(III) acids and their derivatives, a reaction like the Arbuzov does not occur under similar conditions but a more complex process takes place accompanied by fission of the $\rangle As-E$ (E = O, S) bond.

The inability of esters of As(III) acids to react with halogen derivatives in a manner like their phosphorus analogues is evidently explained by the reduction of nucleophilicity on going from phosphorus to arsenic.[6] The significantly higher sensitivity of the arsenic atom to the inductive effect of substituents is an important circumstance.[37] Of the possible types of esters of As(III) acids, viz. $R_2As(OR')$, $RAs(OR')_2$ or $As(OR')_3$, only the esters of arsinous acid $R_2As(OR')$ display a clearly marked ability to react with alkyl halides. For the corresponding phosphorus derivatives with the Arbuzov reaction proceeds both with esters of phosphinic acids and with full phosphites, although at different rates. It may be proposed that with phosphorus the reduction in electron density is compensated to a greater extent than with arsenic by the attraction of the unshared electron pair of the oxygen of the alkoxy groups to the *d* orbitals of the central atom. At the same time, in spite of the abundant literature proposing conjugation with the *d* orbitals of the phosphorus atom, a fairly sound view exists on the insignificant role of similar effects in bond formation.[38] In this connection, as an alternative, it would have been useful to clarify the possibility of displaying an α-effect ("supernuclophilicity") as a feature inherent to certain phosphorus derivatives in contrast to the arsenic-containing analogues. The presence of an unshared electron pair on the atom connected directly to the nucleophilic centre is, as is known,[39,40] one of the most important factors determining the order of the nucleophilicity. However there are no literature data capable of successfully confirming a deviation from the Brønsted rule for esters of P(III) acids.

Among the other reasons explaining the difference in behaviour of esters of P(III) and As(III) acids it is impossible not to mention the unique nature of the phosphorus–oxygen bond in the phosphoryl group arising in reactions of this type. The high thermodynamic stability of this bond (estimated at 552 kJ/mol) is one of the driving forces of the Arbuzov reaction (the strength of the As–O bond is estimated at 443 kJ/mol [41]). Finally new E–C bonds arising in the course of side reactions, when E = P, prove to be more stable (for example by 40.2 kJ/mol), while the fissile E–OC bonds in esters of

As(III) acids are more labile. The latter circumstance superimposes a special imprint on the properties of these esters, imparting to them, in contrast to the phosphorus analogues, an increased hydrolytic instability, but the intermediate product containing an alkoxy group on the arsenic atom is susceptible to a different sort of side reaction, complicating significantly the course of the reaction.

Evidently these same special features may explain the more marked inclination of tetracoordinated arsenic derivatives to conversions occurring with a reduction in valency.

III. The retro-Arbuzov reaction in organic derivatives of As(V)

1. Reactions of compounds containing an arsenyl group

The first information on the possibility of conversions of esters of tetracoordinated arsenic acids occurring with a reduction of its valency were known even before the discovery by A E Arbuzov of the reaction bearing his name.

Even in 1867 Kraft[2] showed that reduction of arsenic to the trivalent state occurred on heating a mixture of arsenic acid with tetraethoxysilane to 230 °C.

However only in 1947 did Komissarov and collaborators[42] realise that the conversion of esters of alkylarsonic acids on heating to a temperature of the order of 200 °C was similar to the process occurring in the reverse direction to the Arbuzov reaction

$$CH_3As(O)(OCH_3)_2 \rightarrow (CH_3O)_3As.$$

The isomerisation was accompanied by the formation of alcohols and a fraction in which the arsenic content was higher than in the corresponding trialkyl arsenites.

These studies appear to be the starting point for the investigations of more recent times on the possibility of achieving conversions with the oxygen derivatives of tetracoordinated arsenic proceeding in a direction opposite to the Arbuzov reaction.

In reality a wider study of the behaviour of trialkylarsine oxides[4] and esters of dialkylarsinic and alkylarsonic acids[2,4] at temperatures close to 200 °C confirmed the conclusions on the thermal instability of oxygen derivatives of As(V). Certain features linked primarily with the fairly complex character of the conversions were clarified.

On pyrolysis of esters of alkylarsonic acids, in addition to the isomerisation product (I) [2,4] the yield of which proved to be generally insignificant and rarely exceeded 10%. The formation was observed of reduction products, viz. the corresponding esters of alkylarsonous acids (II).

$$RAs(O)(OR)_2 \xrightarrow{\Delta} \begin{cases} \rightarrow (RO)_2As \text{ (I), 2—11\%} \\ \rightarrow RAs(OR)_2 \text{ (II), 6—40\%} \end{cases}$$

The authors also indicated the formation in the reaction of an alcohol with the residue of the alkoxy group of the initial ester. On pyrolysis of the dibutyl ester of methylarsonic acid the presence was detected of a carbonyl compound which reacted with 2,4-dinitrophenylhydrazine.[4]

The esters of diethylarsinic acids proved to be even less stable to heat and decomposed with resinification even on attempted distillation.[2,4] It is necessary to record that the formation of isomerisation products was hardly observed by the authors in this case. In addition to the reduction products, viz. the corresponding esters of dialkylarsinous acids, alcohols containing the hydrocarbon residue of the alkoxy group and also dialkylarsinic acids were successfully identified. The dibutyl ester of ethylarsonic acid was isolated in 8% yield from the products of oxidation of the butyl ester of diethylarsinous acid as a result of thermal decomposition.

The main products of the pyrolysis of tertiary arsine oxides, as has been clarified,[4] are also reduction products, viz. the corresponding tertiary arsines and alcohols. The formation in small quantities of isomerisation products, esters of dialkylarsinous acids, was observed.

$$R_3AsO \xrightarrow{\Delta} \begin{cases} \rightarrow R_3As, ROH \\ \rightarrow R_2AsOR \end{cases}$$

The authors considered a disproportionation reaction probable, since tributylarsine was isolated from the pyrolysate of methyldibutylarsine oxide.

A more detailed investigation of the thermal conversions of derivatives containing the arsenyl group indicated the complexity of the processes taking place. The yield of isomerisation products was, as a rule, below 10%, a significant proportion of the starting material resinified.

A higher yield of isomerisation products (32—46%) was observed in the pyrolysis of the diethyl ester of ethylarsonic acid and the dibutyle ester of butylarsonic acid obtained by the method of esterification.[3,4] The authors came to the conclusion that admixture of selenium compounds, used previously to obtain the initial As(V) esters, catalyses oxidation—reduction side reactions accompanying the isomerisation. It was shown by thermography that the reaction proceeds in one stage and, depending on the character of the environment of the arsenic atom, the temperature for the initiation of conversion (TIC) varied within the limits 115—282 °C. The TIC increased with an increase in the length and branching of the hydrocarbon substituents. From the thermographic data a stability series at increased temperature was drawn up for the esters as a function of the structure of the hydrocarbon residue bound to the arsenic atoms.

$$(CH_3)_2CHCH_2 > C_4H_9 > C_2H_5 > CH_3 > C_6H_5CH_2 > CH_2{=}CHCH_2 > (CH_3)_2CH.$$

Subsequent investigations of the retro-Arbuzov reaction in esters of arsinic acids showed that on adding small quantities of electrophilic reagents (alkyl halides, salts and acids) conversion began at lower temperatures and the yield of products grew to 50—63%.[3,4] Thermographic data indicated a two-stage process and the absence of an effect on adding nucleophilic reagent (sodium ethoxide, pyridine) on the temperature for the initiation of conversion. An increase of two orders of magnitude in the specific conductivity on mixing the reactants indicated the formation of an ionic intermediate.

A study of the kinetics of the isomerisation of esters of alkylarsonic acids by alkyl halides[3] indicated the overall second order of the reaction which, together with the results of

thermographic investigations,[3,4] afforded the conclusion that the conversion occurred in the opposite direction to the Arbuzov reaction.

$$R(OR')_2AsO+R''X \rightleftharpoons [RAs(OR')_2(OR'')]^{\oplus}+X^{\ominus} \rightarrow$$

$$\rightarrow (R'O)_2AsOR''+RX.$$

Later, similar conversions were investigated for esters of dialkylarsinic acids.[1,43] Here the addition of alkyl halides also reduced the TIC significantly. The use of GLC enabled a more complete analysis of the products formed. When relatively less stable $As-C_{Alk}$ bonds were absent from the initial esters the main route of the process was an exchange of hydrocarbon residues between the alkoxy group and the alkyl halide if the reaction was carried out under conditions when the volatile products formed were continuously distilled out (yield 75–95%).

$$(C_6H_5)_2As(O)OR+R'Hal \rightarrow (C_6H_5)_2As(O)OR'+RHal,$$
$$(C_6H_5)As(O)(OR)_2+R'Hal \rightarrow (C_6H_5)As(O)(OR)(OR')+RHal,$$
$$R'=CH_2C_6H_5;\ Hal=Br;\ R=C_3H_7.$$

The following processes, which the authors regard as oxidation–reduction, occur in parallel

$$(C_6H_5)_2As(O)OR + C_6H_5CH_2Br \xrightarrow[-HBr]{} (C_6H_5)_2AsOR + C_6H_5C(O)H,$$
$$C_6H_5As(O)(OR)_2 + C_6H_3CH_2Br \xrightarrow[-HBr]{} C_6H_5As(OR)_2 + C_6H_3(O)H.$$

This reaction course predominates when R = $C_6H_5CH_2$ although it requires more forcing conditions. Triphenylarsine also appears in the reaction products, which the authors link with the disproportionation.

$$3(C_6H_5)_2AsOCH_2C_6H_5 \rightleftharpoons 2(C_6H_5)_3As+(C_6H_5CH_2O)_3As.$$

In the case of esters containing the less stable $As-C_{Alk}$ bonds the predominant reaction route is retro-Arbuzov accompanied by symmeterisation and exchange processes.

$$Alk_2As(O)OR + R'Br \xrightarrow{-RBr} Alk_2As(O)(OR') \xrightarrow[-AlkBr]{\sim 10\%} AlkAs(OR)(OR') \rightleftharpoons AlkAs(OR)_2 + AlkAs(OR')_2$$
$$\sim 65\%$$

The authors came to the conclusion that irrespective of the nature of the isolated products the first stage of the reaction is the formation of the corresponding alkoxyarsonium salt (V).

$$R_2As(O)OR' + R''CH_2Hal \rightarrow [R_2As(OCH_2R'')OR']^{\oplus}Hal^{\ominus}$$
(III) (IV) (V)

The formation of this salt is confirmed by the increase in conductivity on mixing the reactants (III) and (IV).

The further conversions of the intermediate (V) are determined by the nature of the reaction participants and conditions.

$$(V) \xrightarrow[-RHal]{a} RAs(OR')(OCH_2R'') \rightleftharpoons RAs(OR')_2 + RAs(OCH_2R'')_2$$
$$(V) \xrightarrow[-R'Hal]{b} R_2As(O)OCH_2R'' \xrightarrow{-R''CHO} R_2AsOR'$$
$$(V) \xrightarrow[-R''CHO]{c} R_2AsOR'$$

R=Alk, Ar; R′=Alk; R″=Alk, Ar.

Route *a* (retro-Arbuzov reaction) is most characteristic for esters containing an alkyl group on the arsenic atom. When alkyl groups are absent (R = Ar) route *b* predominates if conditions are created for displacing the equilibrium by removing the more volatile alkyl halide formed. In the opinion of the authors[1,43] an increase in temperature favours the oxidation–reduction reaction (route *c*). In esters having only one $As-C_{Alk}$ bond the retro-Arbuzov reaction may therefore be the main route for conversion under appropriate conditions.

A different situation is generated in attempts to effect the retro-Arbuzov reaction with tertiary arsine oxides. As was explained, on reacting triethylarsine oxide with isopropyl and isobutyl iodide a crystalline compound is formed, the analysis of which indicated a composition $C_{12}H_{31}As_2O_2I$, in place of the expected esters of arsinous acids.[44] Initially the obtained product was assigned the structure of triethyl(triethylhydroxyarsoxy)arsonium iodide.

$$(C_2H_5)_3As-O-As^{\oplus}(C_2H_5)_3.\ I^{\ominus}$$
$$OH$$

However it was subsequently shown that a more precise structure for the reaction products assumes the presence of a symmetrical intramolecular hydrogen bond.[7,44]

$$[R_3AsO\ldots H\ldots OAsR_3]I.$$

A detailed investigation of the kinetics of this reaction was carried out using as example the reaction of triphenylarsine with butyl iodide.[45] The overall order of the reaction proved to be 3 with a partial order of 2 with respect to the initial oxide. In the case of diethyl-4-dimethylaminophenylarsine, for which the formation of a hydroxyarsonium salt $[R_2R'AsOH]I$ [R = C_2H_5, R′ = n-$(CH_3)_2NC_6H_5$] was observed on reaction with butyl iodide in place of the adduct $(R_2R'AsO)_2HI$, processing the kinetic data according to a second-order equation gave consistent rate constants. In spite of the drop in the overall reaction order, the authors explain such a reaction course by more profound conversions and the increased basicity of the initial oxide.[7,44]

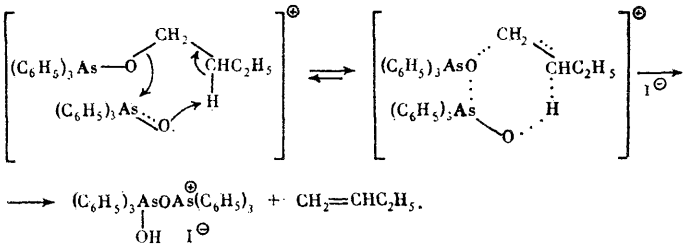
Of several possible schemes explaining the formation routes of adducts of type $(R_2R'AsO)_2HX$ in the reaction of tertiary arsine oxides with alkyl halides, the authors decided upon Scheme 3

assuming the intermediate formation of an alkoxyarsonium salt capable of being later converted by an irreversible reaction (Scheme 4) to the final products.[44,45]

Scheme 3

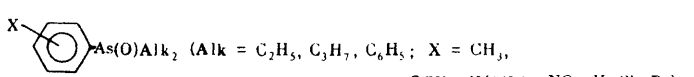
$$(C_6H_5)_3AsO + ICH_2CH_2C_2H_5 \rightleftharpoons \left[(C_6H_5)_3AsO\ldots\underset{\displaystyle CH_2C_2H_5}{\overset{\displaystyle |}{CH_2}}\ldots I\right] \rightleftharpoons$$
$$\rightleftharpoons [(C_6H_5)_3AsOCH_2CH_2C_2H_5]^{\oplus} + I^{\ominus}$$

Scheme 4



$$\longrightarrow (C_6H_5)_3AsO\overset{\oplus}{As}(C_6H_5)_3 + CH_2{=}CHC_2H_5.$$
$$\quad\ \ OH\ \ I^{\ominus}$$

As was shown by further investigations,[44,46] the adducts of type $(R_2R'AsO)_2HHal$ are formed when using a fairly wide range of reactants. Alkyl halides RHal of normal and branches structure (R = CH_3, C_2H_5, n = C_3H_7, n-C_4H_9, iso-C_4H_9, $CH_2C_6H_5$; Hal = I, Br, Cl) have been used in reactions with trialkylarsine oxides Alk_3AsO (Alk = CH_3, C_2H_5, n-C_3H_7, cyclo-C_6H_{11}) and also with a series of dialkylarylarsine oxides.



The formation of hydroxyarsonium salts in place of 2 : 1 adducts occurred only in certain cases. Attempts have been made to show that hydroxyarsonium sals result from the decomposition of these adducts.[7,44]

$$(R_3AsO)_2HI \rightarrow [R_3AsOH]I + R_3AsO.$$

However the similar conversion was unsuccessful. This compelled the authors to acknowledge that it is impossible to explain the isolation of hydroxyarsonium salts in the reactions of tertiary arsine oxides with alkyl halides by more profound conversions and that the reason for the appearance of these salts remains unclear.

When analysing the first results obtained on investigating the conversions of tertiary arsine oxides by alkyl halides it is important to note that in the overwhelming majority of cases only alkyl iodides are used in these reactions[44–46] but the yield of crystalline products, as a rule, is far from quantitative. Only for trimethyl- and triethylarsine oxides reacting with methyl iodide was the yield 61.7 and 65.6% respectively while in all the remaining cases it varied between 25 and 50%.

Analysis of the gaseous reaction products indicated the formation of olefins, which is in agreement with the proposed Scheme 4. However on using methyl iodide, the presence of methane and ethane was recorded in addition to ethylene.[7] This indicates the presence of side reactions.

The problem of the composition of the liquid portion of the reaction mixture, in which the products of a retro-Arbuzov reaction would be sought, remained on one side for some time. This may be explained by the unexpected formation of crystalline products of unusual structure such as $(R_2R'AsO)_2HHal$. Only later was it discovered that on reacting diethylphenylarsine oxide with alkyl bromides were esters of ethylphenylarsinous acid isolated in up to 70% yield.[47] It was therefore shown possible to effect a conversion opposite to the Arbuzov reaction for certain tertiary arsine oxides.

$$(C_2H_5)_2(C_6H_5)AsO + AlkBr \rightarrow$$
$$\rightarrow [(C_2H_5)_2C_6H_5AsOAlk]Br \rightarrow (C_2H_5)(C_6H_5)AsOAlk + C_2H_5Br$$
$$Alk = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4A_9.$$

Somewhat later an analogous route for the reaction was also reported for trialkylarsine oxides (the yield of esters was only ~10%).[48] However the closeness of the boiling points of the reaction products did not enable results to be obtained which could be acknowledged to be sufficiently clear.

Subsequent investigations were performed using diphenylalkylarsine oxides.[49] First of all evidence was obtained that this reaction may be carried out as the main process accompanied by the formation of esters of diphenylarsinous acid in 65% yield.

$$(C_6H_5)_2RAsO + AlkX \rightarrow (C_6H_5)_2AsOAlk + RX,$$

$$R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9;\ Alk = CH_3,\ C_2H_5,$$

$$n\text{-}C_3H_7,\ n\text{-}C_4H_9;\ X = Br,\ I$$

The most important feature of these conversions is the formation of the corresponding haloarsines, which was noted for the first time, together with the esters of diphenylarsinous acid.[11,49]

Triphenylarsine oxide, containing no akyl groups capable of being split off by activated halogen derivatives of the type $HalCH_2Z$ (where Z = $C(O)OCH_3$, $C(O)OC_2H_5$, CN, $C(O)CH_3$; Hal = Cl, Br) forms hydroxyarsonium salts $[Ph_3AsOH]Hal$ ($Ph_3AsO.HHal$) (1 : 1) in place of adducts of composition $(Ph_3AsO)_2HHal$ (2 : 1).[50]

Similar hydroxyarsonium salts were isolated on using the usual alkyl bromides under more forcing conditions.[50] This suggested that the formation of 2 : 1 adducts such as $(Ph_3AsO)_2HHal$ or 1 : 1 adducts like $Ph_3AsO.HHal$ is determined by the nature of the halogen in the initial halogen derivative.

These facts together with the possibility mentioned above of forming haloarsines as side products enabled the following hypotheses to be put forward:

—the first stage of the process is the formation of an alkoxyarsonium salt $[R_2R'AsOAlk]Hal$ irrespective of the nature of the products isolated:

—the appearance of adducts $(R_2R'AsO)_2HHal$ is the result of the reaction of the hydroxyarsonium salt $[R_2R'AsOH]Hal$ with the initial oxide $R_2R'AsO$;

$$R_2R'AsO + [R_2R'AsOH]Hal \rightarrow (R_2R'AsO)_2HHal$$

—the hydroxyarsonium salts themselves appear as a result of the decomposition or hydrolysis of the intermediate alkoxyarsonium salts;

$$R_2R'AsO + AlkHal \rightarrow$$
$$\rightarrow [R_2R'AsOAlk]Hal \begin{cases} \xrightarrow{H_2O} [R_2R'AsOH]Hal + AlkOH \\ \xrightarrow{\Delta} [R_2R'AsOH]Hal + \text{olefin} \end{cases}$$

—the isolation of haloarsines together with esters of trivalent arsenic acids in those cases when a reverse Arbuzov reaction occurs is linked with the decomposition of thermally unstable hydroxyarsonium salts formed as side products:

$$[R_2R'AsOH]Hal \xrightarrow{\Delta} RR'AsHal.$$

The central point of these conversions is the formation in the first stage of an alkoxyarsonium salt $[R_2R'AsOAlk]Hal$ as an intermediate. Attempts to isolate these salts in the reactions of tertiary arsine oxides with alkyl halides were unsuccessful. The difficulty of isolating byproducts is explained by their instability linked with the increased reactivity of the alkoxyarsonium cation.[1,3,4,7]

Nevertheless the reduction of the positive charge on the arsenic atom in the cation by replacing phenyl by alkyl, the introduction of a less nucleophilic bromide anion and the use of carefully dried solvents and apparatus enabled the formation of an alkoxyarsonium salt to be recorded in one of the examples.[51]

$$(n\text{-}C_3H_7)_3AsO + C_2H_5Br \rightarrow [(n\text{-}C_3H_7)_3AsOC_2H_5]Br$$

Confirmation was also obtained for the other hypotheses in a similar manner. The synthesis and study of the thermal conversions of hydroxyarsonium salts was the subject of a special investigation.[52]

These results enabled an overall Scheme to be drawn up for the conversion of tertiary arsines by alkyl halides as a single process, the route of which is determined by the environment of the arsenic atom.[53–55]

Scheme 5

$$R_2R'AsO + R''X \longrightarrow [R_2R'AsOR'']X$$
$$[R_2R'AsOR'']X \begin{cases} \xrightarrow[-RX]{a,\ X^{\ominus}} R_2AsOR'' \rightleftharpoons R_3As + RAs(OR'')_2 \\ \xrightarrow[-\text{olefin}]{b,\ R_2R'AsO} [R_2R'AsOH]X \xrightarrow{R_2R'AsO} (R_2R'AsO)_2HX \end{cases}$$
$$[R_2R'AsOH]X \xrightarrow{-ROH} (RR'As)_2O \xrightarrow{R''X} RR'AsOR'' + RR'AsX$$

The more basic trialkylarsine oxides (R = R′ = Alk) react predominantly as bases undergoing dehydrohalogenation of the alkyl halide (Scheme 5, route *b*). If the retro-Arbuzov reaction (Scheme 5, route *a*) also takes place under these conditions then it is only a side reaction. In the case of the less basic dialkylphenyl- and alkyldiphenylarsine oxides (R = Alk, R′ = C_6H_5, R′ = Alk) the contribution of route *a*, leading to a retro-Arbuzov reaction product, is significantly increased and route *b* plays the role of a side reaction. Route *b* remains the sole possible route in the case of triphenylarsine oxide, which contains no $As-C_{Alk}$ bond capable of fission.

The Scheme represented above for the conversion of tertiary arsine oxides by halogen derivatives enables the available data to be combined, considering them as different aspects of a single fairly complex and interconnected process, certain steps of which are worthy of further study. Processes of elimination, which frequently accompany nucleophilic substitution are of particular interest in this connection. The possibility of α- and β-elimination of alkoxyarsonium salts arising in the intermediate stage was investigated in special experiments using triphenylarsine oxide.[56] The detection of tertiary arsines, olefins and aldehydes in the reaction products indicates the need to take the side reactions into account although their contribution may prove to be small (~6–10%).

2. The retro-Arbuzov reaction with tertiary arsine sulphides

Tertiary arsine sulphides are the sole representatives of the thioarsenyl compounds for which the conversions occurring with a reduction in the valency of the arsenic atom have been investigated at the present time. This may explain the unsuccessful attempts to synthesise esters of tetracoordinated arsenic containing a $\rangle As(S)$ group, although here definite progress has been planned for some time past.[57–59]

The first information on the pyrolysis of tertiary arsine sulphides was published in 1966.[60] As was explained, the pyrolysis of diethylphenylarsine sulphide in a sealed tube and in vacuum leads to the formation of an isomerisation product in 6–9% yield.

$$(C_2H_5)_2C_6H_5AsS \xrightarrow{200-240^{\circ}\ C} (C_6H_5)(C_2H_5)AsSC_2H_5.$$

The thermal decomposition of trialkylarsine sulphides proceeds in a similar manner. On heating triethyl-, tripropyl- and methyldipropylarsine sulphides in vacuum at 200 °C for 1 h the corresponding esters of dialkylthioarsinous acids were obtained in 20–26.8% yield.[60,61] The isolation of other pyrolysis products was not reported although the formation of a complex reaction mixture was obvious, as on the pyrolysis of the oxides.

An investigation of the decomposition of triethylarsine sulphide by DTA with simultaneous recording of the conductivity change showed the presence of two exo effects.[61] The position of the first of them coincided in time with an increase in conductivity. It was concluded that heterolytic fission of an As–C bond occurred with the subsequent formation of a thioether.

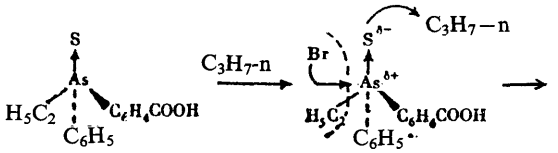
$$(C_2H_5)_3AsS \xrightarrow{\Delta} [(C_2H_5)_2As^{\ominus}S + {}^{\oplus}C_2H_5] \longrightarrow (C_2H_5)_2AsSC_2H_5.$$

Similar results were obtained on investigating the thermal isomerisation of tripropyl-, and methyldipropyl- and diethylphenylarsine sulphides by DTA.[5,8,61]

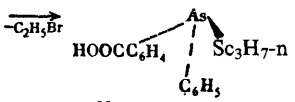
As was clarified by subsequent investigations the addition of small quantities (up to 0.1 mol) of alkyl halides and salts to tertiary arsine sulphides leads to an appreciable reduction in the temperature for the initiation of conversion.[5,8,62] The yield of product of the retro-Arbuzov reaction thereby grows significantly. The ester of

propylphenylthioarsinous acid was isolated in 60% yield by the reaction of a 1:1 ratio of ethyl bromide and dipropylphenylarsine sulphide at 100 °C for 2.5 h. Trialkylarsine sulphides are converted by alkyl halides into the corresponding thioesters in 25–67% yield.[8,62]

The retro-Arbuzov reaction was used for a series of tertiary arsine sulphides with the aim of obtaining asymmetric esters of the RR'AsSR'' type.[63] A change in the rotation of the initial (enantiomeric) sulphides to the opposite sign was recorded.



$[\alpha]_D^{20} + 19{,}12$



$[\alpha]_V^{20} - 3{,}18$

It should be noted that the esters of thioarsinous acids were not the only products isolated in the course of the retro-Arbuzov reaction with tertiary arsine sulphides. In several cases the formation was noted of the corresponding monohaloarsines as byproducts, the content of which grew with an increase in temperature, in contact time and on going from alkyl bromides to iodides.[5,8,62,64]

On reacting ethylphenyl-α-naphthylarsine sulphide with methyl iodide, diethyl-α-naphthylarsine, α-naphthyldiphenylarsine sulphide and free sulphur were isolated in addition to the corresponding ester of thioarsinous acid.[65]

The synthesis of the alkylthioarsonium salts formed as intermediates was carried out to confirm the two-stage nature of the retro-Arbuzov reaction.[66]

$$R_2R'AsS + AlkX \rightarrow [R_2R'AsSAlk]X,$$

R, R', Alk=C_2H_5, C_3H_7, C_4H_9, C_6H_5; X=Br.

The corresponding esters of thioarsinous acids were successfully obtained in up to 50% yield by the decomposition of these salts.

The retro-Arbuzov reaction was also observed for several tertiary arsine sulphides on using organic acids, their anhydrides and halogen derivatives as electrophilic reagents.[67,68]

$$Alk_2C_6H_5AsS + RC(O)X \longrightarrow [Alk_2C_6H_5AsSC(O)R]X \xrightarrow{-AlkX} \longrightarrow AlkC_6H_5AsSC(O)R,$$

Alk=C_2H_5, C_3H_7, C_4H_9; R=CH_3, C_2H_5, C_3H_7, CH_2Cl, $CHCl_2$, CCl_3; X=OH, RC(O).

When using carbon tetrachloride and alkyl chloroformates as electrophiles the authors also proceeded from an analogous reaction scheme.

$$R_2R'AsS + R''Cl \rightarrow [R_2R'AsSR'']Cl \rightarrow \rightarrow RR'AsSR'' + RCl,$$

R, R'=Alk, Ar; R''=CCl_3, $CH_2C(O)OCH_3$

A more complex character was noted for the conversions indicated requiring their further study.

The reaction of tertiary arsine sulphides with acid chlorides has been investigated in a fairly detailed manner.[69–71] On carrying out the reaction with acetyl chloride in a solvent, either the thioacetylarsine (VIII) (in benzene)[8] or the acetylthioarsonium chloride (VII) (in acetone) were formed.[8,70]

$$\underset{(VI)}{R_2R'AsS} + CH_3C(O)Cl \longrightarrow \underset{(VII)}{[R_2R'AsSC(O)CH_3]Cl} \xrightarrow{-RCl} \underset{(VIII)}{R_2R'AsSC(O)CH_3},$$

R=R'=C_2H_5, n-C_3H_7, n-C_4H_9; R'=C_6H_5, R=C_3H_7.

On carrying out the same reaction without a solvent, the corresponding chloroarsines and *S*-alkyl esters of thioacetic acid were isolated.[69]

$$\underset{(VI)}{(C_6H_5)Alk_2AsS} + CH_3C(O)Cl \rightarrow \underset{(IX)}{(C_6H_5)AsAlkCl} + \underset{(X)}{CH_3C(O)SAlk},$$

Alk=C_3H_7, C_6H_{13}.

No thioacetylarsines (VIII) were observed in the reaction products on repeatedly reproducing these experiments.[71] In this case a tertiary arsine dichloride (XI) was isolated in place of the intermediate (VII) and the corresponding chloroarsines (IX) in place of the thioacetylarsines (VIII).

$$\underset{(I)}{R_2R'AsS} + 2CH_3C(O)Cl \longrightarrow \underset{(XI)}{R_2R'AsCl_2} \xrightarrow[-RCl]{\Delta} \underset{(IX)}{RR'AsCl},$$

R=R'=C_2H_5, n-C_3H_7, iso-C_3H_7;

R=CH_3, C_2H_5, n-C_3H_7, R'=C_6H_5.

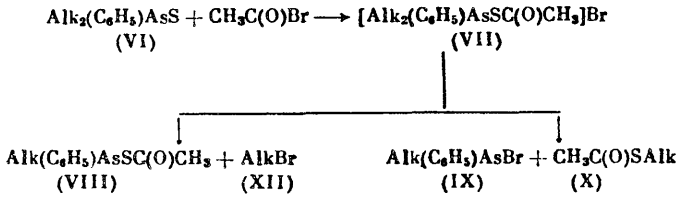
The formation of tertiary arsine dichlorides (XI) has been reported in a whole series of other cases.[72]

$$R_2R'AsS + R''Cl \rightarrow R_2R'AsCl_2,$$

R''=H, COCl, PCl_2, CH_2CN, $CH_2C(O)CH_3$, $C_6H_5C(O)$, $CH_2C(O)OCH_3$.

Considering that similar conversions are also known for teriary arsine oxides,[73] it may be proposed that here also a process alternative to the retro-Arbuzov reaction is taking place, occurring without changing the valency of the arsenic.

Reaction with acetyl bromide leads to the formation of a more complex mixture of products.[69,74]]

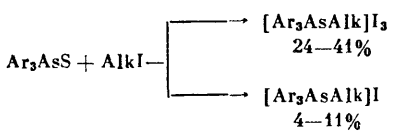


At a 1:1 ratio of starting materials the reaction occurs fairly energetically at room temperature and is completed by the formation of (VIII) and (X) contaminated with alkyl halide (XII). With a 2:1 excess of acetyl bromide and an increase in the contact time the reaction, in the authors' opinion, goes further so that it is not possible to isolate the thioacetylarsine (VIII) in the pure state or its yield is reduced. From this it was concluded that the haloarsine (IX) is formed by secondary conversions.

$$(VIII)+(XII)\rightarrow(IX)+(X)$$

In parallel to the investigations mentioned and independently of them the reaction of tertiary arsine oxides with alkyl halides has been studied by one further group of authors.[75-77]

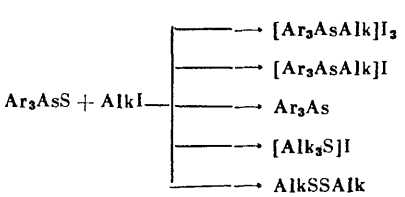
Using as starting materials triarylarsines containing the more stable $As-C_{Ar}$ bonds these authors showed that at an excess of alkyl iodide (1:8, acetone, boiling for 15–50 h) the reaction took place without a change in arsenic valency.



$Ar=C_6H_5$, $CH_3C_6H_4$;

$Alk=CH_3$, C_2H_5, C_3H_7, $CH_2C_6H_5$, $CH_2C(O)OC_2H_5$.

One of the sulphur-containing products, trimethylsulphonium iodide, was successfully isolated in 6% yield in the case of triphenylarsine sulphide and methyl iodide. In addition it was suggested that dialkyl disulphides and tertiary arsines were present in the reaction mixture. The results of the reaction of triarylarsine sulphides with alkyl halides may be expressed by the following scheme.



It is important to note that in the experiments mentioned only the most reactive alkyl halides were used since the application of alkyl bromides led to the isolation of unreacted starting sulphide.

The trialkylarsine sulphides proved to be more reactive in alkylation reactions. Alkylthioarsonium salts are formed fairly rapidly on reaction under mild conditions.

$$Alk_3AsS+RX\rightarrow[Alk_3AsSR]X,\quad {}_{23-88\%}$$

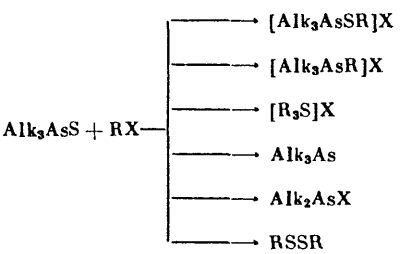
$Alk=C_2H_5$, n-C_3H_7 cyclo-C_6H_{11};

$R=CH_3$, C_2H_5, n-C_4H_9; X = Br, I

Under more forcing conditions the quaternary arsonium salt, containing no sulphur, was isolated once again.

$$(C_2H_5)_3AsS+RI\rightarrow[(C_2H_5)_3AsR]I,$$
$$R=CH_3,\ C_2H_5.$$

The impossibility of isolating the corresponding triiodides is explained by their solubility in the reaction mixture. Attempts to identify the sulphur-containing products gave no clear results. Only in the case of methyl iodide was trimethylsulphonium iodide successfully isolated from the reaction mixture. On reacting triethylarsine sulphide with n-propyl bromide a broad fraction was obtained containing, in the authors' opinion, bromodiethylarsine, triethylarsine and di-n-propyl sulphide. The data obtained indicate the formation of an even more complex mixture in the reaction of trialkylarsine sulphides with alkyl halides.



The crystalline reaction products were isolated and identified, the liquid products were not successfully separated. The formation of the latter was confirmed only indirectly. Quaternary arsonium salts may arise from trialkylarsines and sulphonium salts from dialkyl disulphides.

Comparison of the composition of the products isolated on alkylation of triaryl- and trialkylarsine sulphides indicates that these reactions have a general character. The main differences are the possibility of breaking the As–C bond in the case of trialkylarsine sulphides (haloarsine formation) and also the appearance in this case of the intermediately formed trialkyl(alkylthio)arsonium salts. Difficulties linked with the isolation of the analogous triaryl-(alkylthio)arsonium salts are explained by the authors by the stability of these salts due to the electron-accepting action of the phenyl groups and the high nucleophilicity of the anion. In fact triphenyl(ethylthio)arsonium tetrafluoroborate proved to be a completely stable compound. Addition of a carrier of more nucleophilic anions, such as sodium iodide, to a solution of this compound in acetone led to decomposition of the salt due to the reduction of its stability.

$$[(C_6H_5)_3AsSC_2H_5]BF_4+NaI\rightarrow[(C_6H_5)_3AsOH]I+$$
$$+[(C_6H_5)_3AsOH]I_3+(C_6H_5)_3As.$$

Similar observations enabled the important conclusion to be drawn that an alkylthioarsonium salt is stable if one of two factors are present. Either the anion has a low nucleophilicity or the substituents bound to the arsenic atom have a small electronegativity. This conclusion was confirmed by the synthesis of a whole series of fairly stable trialkyl- and triarylthioarsonium salts containing an anion of reduced nucleophilicity (BF_4^-, $CH_3SO_4^-$).

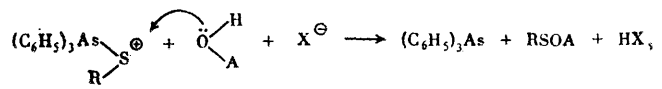
$$R_3AsS+[Alk_3O]^{\oplus}BF_4^{\ominus}\rightarrow[R_3AsSAlk]^{\oplus}BF_4^{\ominus}+Alk_2O,$$
$$R_3AsS+(CH_3)_2SO_4\rightarrow[R_3AsSCH_3]^{\oplus}CH_3SO_4^{\ominus},$$
$$R=CH_3,\ C_2H_5,\ C_3H_7,\ \text{cyclo-}C_6H_{11},\ C_6H_5;$$
$$Alk=C_2H_5,\ C_4H_9.$$

The preparation of a whole series of alkylthioarsonium halides and more stable representatives of these salts containing anions of reduced nucleophilicity was a turning point in the investigation of the features of carrying out the retro-Arbuzov reaction with tertiary arsine sulphides. The study of the structure and properties of the alkylthioarsonium salts was an important step in this investigation.[77,78] As was clarified, alkylthioarsonium salts in acetone behave as weakly associated electrolytes with fairly high specific conductivity values. This indicates their ionic structure. The action of nucleophiles depends on their nature and on the character of the environment of the arsenic atom. Thus trialkyl(alkylthio)arsonium salts are isolated unchanged after extended contact with water and alcohols at 50–60 °C. Triphenyl(alkylthio)arsonium tetrafluoroborates give triphenylarsine (70–97%) and the complexes 2 $(C_6H_5)_3AsO.HBF_4$ (40–82%) on hydrolysis and the complex $(C_6H_5)_3AsO.BF_3$ on alcoholysis.

Amines, being stronger nucleophiles, react fairly rapidly at ordinary temperatures irrespective of the environment of the arsenic atom.

$$[(C_6H_5)_3AsSC_2H_5]BF_4+(C_2H_5)_2NH\rightarrow(C_6H_5)_3As+\underset{85-89\%}{[(C_2H_5)_2NH_2]BF_4}$$
$$[(C_2H_5)_3AsSC_2H_5)Br+(C_2H_5)_3N\rightarrow\underset{90\%}{[(C_2H_5)_3NH]Br}$$

The authors considered the possibility of attack by the nucleophile at the sulphur atom

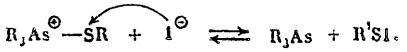


$$2RSOA\rightarrow RSSR+AOOA,$$
$$(C_6H_5)_3As+AOOA\rightarrow(C_6H_5)_3AsO+AOA,$$
if A=H, then $(C_6H_5)_3AsO+HX\rightarrow[(C_6H_5)_3AsO]_2HX.$

The notion of attack by the nucleophile at the sulphur atom is also attractive for explaining the results obtained on reacting tertiary arsine sulphides with alkyl halides.

Scheme 6

$$R_3AsS+R'I\rightarrow[R_3AsSR']^{\oplus}I^{\ominus}, \quad (1)$$



$$R'SI\rightleftharpoons[2R'S^{\bullet}+2I^{\bullet}]\rightleftharpoons R'SSR'+I_2,$$
$$R'SSR'+4RI\rightarrow2[R_3'S]^{\oplus}I^{\ominus}+I_2,$$
$$R_3As+I_2\rightarrow R_3AsI_2,$$
$$2R_3AsI_2\rightleftharpoons R_3As+[R_3AsI]^{\oplus}I_3^{\ominus},$$
$$R_3As+R'I\rightarrow[R_3R'As]^{\oplus}I^{\ominus}.$$

The proposed chain of reactions (Scheme 6) differs appreciably from the Scheme considered previously (see Section III, 2) except for stage (1) which is common..

Thus inconsistencies have been detected in relation to the interpretation of the routes of conversion of the alkylthioarsonium halides generated at the intermediate stage. In reality the results obtained indicate the conversion of the alkylthioarsonium salts to the corresponding thioesters in fairly high yield.[62–66] On the other hand the sequence of interactions proposed (Scheme 6), in which there is no place for thioesters, i.e. the route connected with the existence of the retro-Arbuzov reaction for tertiary arsine sulphides, is considered impossible.[75,76] From the point of view of one group of authors,[75,76] the main reaction products are quaternary arsonium salts $[R_3R'As]Hal$ or $[R_3R'As]Hal_3$ while the formation of such salts is not even mentioned in the communications of another group of authors.[62–66]

Nevertheless, as was clarified, the inconsistencies indicated were not differences in principle since the authors were investigating two sides of the same process. In each case attention was paid to the identification of either the liquid or the crystalline reaction proucts. In any event special investigations were necessary in order to resolve these inconsistencies.[10] It was shown by PMR spectroscopy using alkylthioarsonium tetrafluoroborates that the most probable place for nucleophilic attack in the alkylthioarsonium cation was not the sulphur atom but was the positively polarised carbon atom of the alkyl group on the arsenic.[79] In other words, the decomposition of the alkylthioarsonium salts must be effected as the second stage of the retro-Arbuzov reaction and leads to the formation of thioesters of thioarsinous acids. This posed the problem of finding a method capable of identifying the components of the complex reaction mixture containing derivatives of trivalent arsenic which are close in properties. Gas-liquid chromatography (GLC) was such a method. With the aid of GLC, the presence of esters of thioarsinous acids in the products of the reaction of tertiary arsine sulphides with alkyl halides was unequivocally confirmed and in addition one of the important properties of these esters, viz. their ability to disproportionate, was also confirmed.[80–83]

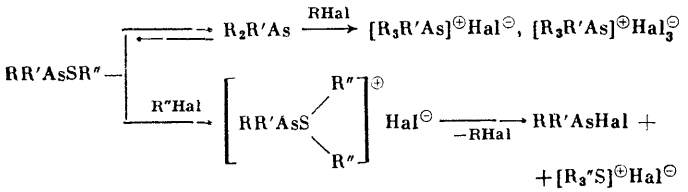
$$2RR'AsSR''\rightleftharpoons R_2R'As+R'As(SR'')_2,$$
$$3RAs(SR'')_2\rightleftharpoons R_3As+2As(SR'')_3,$$
$$R,\ R''=Alk,\ R'=C_6H_5$$

The formation of a tertiary arsine by the disproportionation of thioesters enabled the experimental data concerning the reaction of tertiary arsine sulphides with alkyl halides to be assessed in a new

way. The inconsistencies are successfully eliminated if it is assumed that the formation of the thioesters of arsinuous acids are the main course of the reaction.

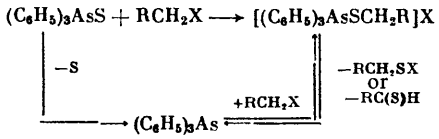
$$R_2R'AsS+R''Hal\rightarrow[R_2R'AsSR'']^{\oplus}Hal^{\ominus},$$
$$[R_2R'AsSR'']^{\oplus}Hal^{\ominus}\rightarrow RR'AsSR''+RHal.$$

Secondary processes linked with the possibility of disproportionation of the thioesters formed or with their alkylation then follow. A similar disproportionation may be the reverse process with an unfavourable position of the equilibrium. However the presence of the alkyl halide binding the tertiary arsine into an insoluble arsonium salt shifts this equilibrium to the right.



The proposed Scheme for the conversions of tertiary arsine sulphides by alkyl halides[81,82] in contrast to that put forward previously[62,76] enables a large number of features of this reaction to be understood, including the reasons for the formation of arsonium and sulphonium salts in addition to the thioesters, and also of haloarsines and tertiary arsines. At the same time this Scheme must not be considered final. In any event it is impossible to extend it to triarylarsine sulphides which do not contain a relatively readily fissile $As-C_{Alk}$ bond and consequently may not be converted into the corresponding thioesters.

It is evident that as a minimum three alternative routes of conversion must be considered in this case.



The relatively high stability of the intermediates in the retro-Arbuzov reaction involving tertiary arsine sulphides enabled a more stepwise investigation of the kinetics of this conversion.[84–86] Conductiometry was used as the method for monitoring the running concentrations of the alkylthioarsonium salts. The high sensitivity of this method enabled investigation of areas of concentration uncomplicated by the reverse reaction and by secondary conversions.

As expected the partial order of the first step proved to be close to one and its overall order close to two. A change from acetone to the more polar dimethyl sulphoxide and propan-1-ol and also replacement of ethyl bromide by the iodide leads to an increase in the reaction rate. The data obtained were interpreted from the position of an S_N2 mechanism. Comparison of these data with the results of investigations of the kinetics of the conversions of tertiary arsine oxides by alkyl halides led to the recognition of the close similarity of the nucleophilic reactivity of the oxides and sulphides.[84] This fact is particularly interesting since the basicities of these two classes of compounds differ quite appreciably.

Later an investigation was carried out of the kinetics of the second stage of the reaction using the decomposition of triethylethylthioarsonium iodide and bromide in acetone.[85,86] Processing the experimental data when calculating the overall salt concentration in the solution did not enable a conclusion to be drawn between a first or second kinetic order for the reaction. In view of the conductimetric data indicating association of the alkylthioarsonium salts in solution,[77,78] the authors proposed that not all the salt, but only the fraction present as an ion pair, is subject to decomposition under the conditions investigated. Processing the results obtained according to a kinetic equation, in which the concentration of ion pairs is expressed through the dissociation constant,[87] confirms the proposals made. It is interesting that other investigators studying the kinetics of the decomposition of alkoxyphosphonium salts are also inclined to the conclusion of the possibility of association through hydrogen bond formation.[88]

IV. Conclusion

In conclusion it may be recorded that the numerous attempts to bring about the Arbuzov reaction in esters of trivalent arsenic acids proved to be unsuccessful. Ideas on the possibility of a simple and unequivocal carrying out of the first stage of this reaction with esters of dialkyl- and alkylphenylarinous acids have not been confirmed. In spite of the difference in interpretation of the routes of forming quaternary arsonium salts as one of the products of the conversions being considered, the conclusion on the appreciable reduction of the nucleophilic reactivity of the esters of trivalent arsenic acids in comparison with their phosphorus-containing analogues undoubtedly seems more important. The reason for this lies in the characteristics of the reaction centres and the differences in character of the effect of substituents in the derivatives of phosphorus and arsenic. This, together with the reduction in strength of the E(O) and E–C (E = P, As) bonds on going from phosphorus to arsenic and the enhanced lability of the As–OR bond, strictly limits the possibility of using the Arbuzov reaction in the chemistry of organoarsenic compounds. The unusually high nucleophilic reactivity of esters of trivalent phosphorus acids singles them out among similar derivatives along the period and group and also determines the amazingly unique nature of the Arbuzov reaction.

Conversions accompanied by a reduction in the degree of coordination of the central atom proved to be more characteristic of the organic derivatives of arsenic. The possibility of effecting a retro-Arbuzov reaction among the oxides and sulphides of tertiary arsines is determined by the special features of the arsenic–heteroatom bond, by its strength, by the basicity of the initial nucleophile and by the presence in them of an $As-C_{Alk}$ bond capable of fission. The investigation of the general rules and distinctive features of these conversions and the reactions accompanying them as a function of the environment of the arsenic atom, of the nature of the electrophilic reagent and the reaction conditions, indicates the complexity of the processes taking place and the need for their further study. Inconsistencies emerging in the first stages of the investigations in this field may be connected with the fact that in a large number of studies either the liquid or the crystalline products of the reaction were examined preferentially, which could not possibly give a complete picture. Investigations in recent years have shown the possiblity of effecting a retro-Arbuzov reaction among tertiary arsine oxides containing just one alkyl group

in the environment of the arsenic atom. The isolation of byproducts from this reaction, such as haloarsines and hydroxyarsonium salts, enabled the character of the processes occurring to be linked with the environment of the arsenic atom. The more basic trialkylarsine oxides react predominantly in the direction of dehydrohalogenation of the electrophilic reactant. The retro-Arbuzov reaction occurs as a competing reaction on going to the less basic oxides of dialkylphenyl- and alkyldiphenylarsines. Due to the absence of alkyl groups capable of fission triphenylarsine oxide reacts as a base under these conditions.

The retro-Arbuzov reaction may be considered as the main process for tertiary arsine sulphides, complicated by secondary conversions of the thioesters formed. The necessary conditions for the retro-Arbuzov reaction are here the participation of a soft electrophile, alkyl halide, and the presence in the initial sulphide of at least one $As-C_{Alk}$ bond. In the case of harder chlorine-containing electophiles (hydrogen chloride, acetyl and benzoyl chlorides), chloroacetonitrile, chloromethyl methyl ether, etc.) the reaction may proceed without a change in the degree of coordination of the arsenic atom and is completed by the formation of tertiary arsine dichlorides or the products of their thermal decomposition, viz. the corresponding chloroarsines.

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