

FULL PAPER

Methods for synthesis of secondary alkylarylsinechlorides and their reactivity

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Secondary dialkyl-, diaryl-, alkylarylsinghalides hold one of the most important places in the hierarchy of various classes of organo-arsenic compounds. These compounds can serve as a key for accessing the synthesis of tertiary arsines, studying their structure, reactivity, stereochemical and biological properties. Secondary substituted mixed alkylarylsinghalides, due to the active halogen atom associated with arsenic, have high reactivity in various chemical substitution reactions. Accordingly, they are a source for obtaining representatives of the next series of organo-arsenic compounds with useful properties to meet the needs of various areas of production. Despite the significant position in the chemistry of organo-arsenic compounds, these substances remain poorly studied and therefore the problem of their study still remains relevant. This work is devoted to the study of literary sources that describe methods for the synthesis of secondary arsinghalides, including the experimental results of the author's research. Based on the analysis of the data obtained, the authors recommend the method he has tested for the synthesis of secondary asymmetric arsinghalides. The work provides a detailed description of the recommended method for the synthesis of ethylarylsine chlorides and gives comparative characteristics of a number of obtained substances, as well as the results of analytical and spectroscopic studies, confirming their compliance with the accepted structures.

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KEYWORDS

Dialkyl; diaryl; alkylarylsinehalides; ethylarylsinechlorides; asymmetric; secondary; tertiary arsines.

Introduction

The study of the reactivity of secondary arsenichalides contributes to the development of synthetic methods, the development of methods for the synthesis of previously inaccessible or hard-to-reach functionally substituted organo-arsenic compounds. Such studies are of great theoretical and practical interest.

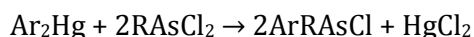
The objective of this research was to study, comparatively characterize, and select the most effective methods for the synthesis of

chiral ethylarylsine chlorides. The objects were secondary arsinghalides to study their reactivity as potential starting products in the synthesis of compounds of three- and four-coordinated arsenic.

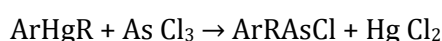
Methods

Secondary arsinghalides have high reactive properties and, with the participation of the chlorine atom, enter into many substitution reactions. Accordingly, they serve as starting products for both symmetrical and

asymmetric tertiary arsines. Diarylarsine chlorides are obtained by the reaction of diarylmercury with arylarsine dichloride

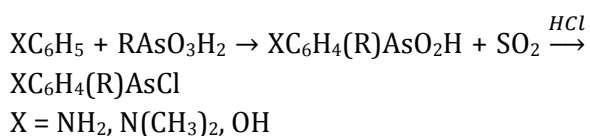


The condensation reaction proceeds with prolonged heating of the mixture. Mixed diarylarsine chlorides are formed when starting products with different radicals are used. The reaction of aromatic organomercury compounds with AsCl_3 also leads to the formation of secondary diarylarsine chlorides [1].



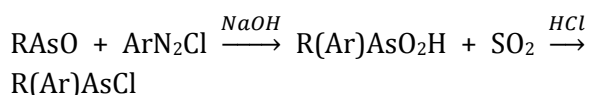
The product yield depends on the chemical nature of the radical. When using radicals having electron-donating substituents in the benzene ring, the yield increases [2].

Mixed alkylarylarsinehalides with functional groups in the benzene ring are obtained by the Meyer method from the corresponding acids by reduction

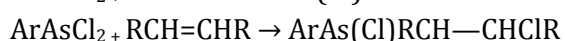
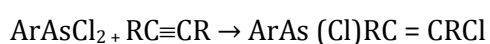


The product yield in this reaction depends on the nature of the halogen contained in the benzene ring, increasing when using the corresponding aryl bromides [3,4].

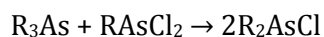
Similarly, asymmetrically substituted secondary arsinghalides can be obtained by the reaction of aromatic arsine oxides with halogen derivatives in an alkaline medium [5-7].



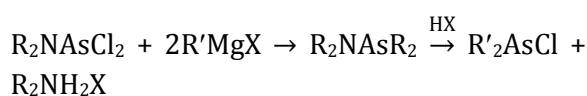
The condensation reaction of primary arylarsine dihalides with unsaturated hydrocarbons of the acetylene and ethylene series leads to the formation of secondary arsinghalides as follows:



As a result of the intrachain chlorination of unsaturated radicals, chlorine derivatives of secondary arylarsine halides form. Dialkyl and diarylarsinghalides can also be obtained by disproportionation of tertiary arsines coordinated by aromatic or aliphatic radicals under the action of arylarsindichlorides [8]:



Another method of obtaining secondary aliphatic and aromatic arsinghalides lies in the action of organomagnesium reagents on dialkylaminoarsindichlorides [9,10].

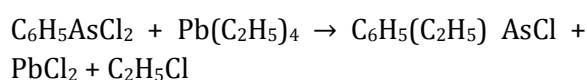


$\text{R}' = \text{alkyl or aryl}; \text{X} = \text{Cl, Br, J}; \text{R} = \text{lower alkyl.}$

During the synthesis of asymmetric secondary arsinghalides with dissimilar radicals, dialkylamino(alkyl)-, dialkylamino(aryl) arsinechlorides are used as the initial arsenic-containing compound. Given the hydrolytic instability of the initial dialkylaminoarsindichlorides, the authors recommend using them in a non-polar solution of AsCl_3 with secondary amines in molar ratios of 1:3 [9].

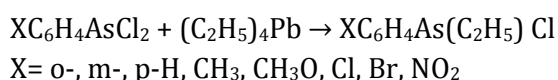
Results and discussion

The considered methods of obtaining secondary arsinghalides are characterized by either their multistage procedure or low yields, or the difficulty of isolating the target products. To obtain asymmetric secondary arsinghalides, the most convenient and effective method is Kamai's method, proposed for the preparation of arsenic compounds containing the ethyl group [3]. The method lies in the interaction of tetraethyl lead with arylarsine dichlorides



We have tested this reaction in the synthesis of asymmetrically substituted ethyl arylarsine chlorides using the reaction of

tetraethyl lead with arylarsine dichlorides containing a large set of substituents in the benzene ring of a different chemical nature [10]:



The reaction proceeds in one stage without the use of solvents, providing a high yield of the target products. The synthesized ethylarylsarsine chlorides by this method (I-XVI, Table 1) are colorless or slightly yellow liquids, well distilled in vacuum. They have a pungent odor that irritates the respiratory

tract. Purification of ethyl-o-,m-,p-nitrophenylarsine chlorides was carried out by precipitation from hexane, since vacuum distillation in an inert gas (nitrogen) atmosphere leads to an explosion. Ethylarylsarsine chlorides are fairly stable during storage under normal conditions and are readily soluble in many organic solvents.

The obtained physical characteristics of ethylarylsarsine chlorides, as well as the atomic refraction of arsenic (on average, 11.72) are fully consistent with the known literature data.

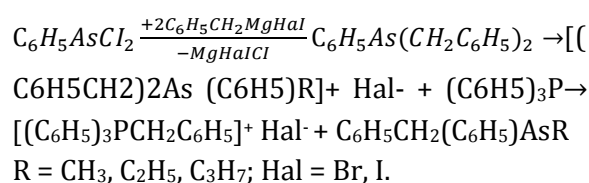
TABLE 1 Ethylarylsarsine chloride XC₆H₄(C₂H₅)AsCl (I-XVI)

№	X	B.T., °C -P mmHg	d ²⁰ ₄	n ²⁰ _D	MR _D		AR _D , As	Formula	Out put %	As, %	
					Found	Calculated				Found	Calculated
I	p-H	91-2/0	1.3985	1.5966	52.71	41.51	11.20	C ₈ H ₁₀ AsCl	63	34.57	34.64
II	p-CH ₃	112/1	1.3295	1.5917	58.63	46.13	12.50	C ₉ H ₁₂ AsCl	71	32.38	32.53
III	p-Cl	171-2/2	1.3298	1.6030	59.41	46.37	12.04	C ₈ H ₉ AsCl ₂	82	29.74	29.88
IV	p-Br	190/2	1.7314	1.6265	60.45	49.27	11.18	C ₈ H ₉ AsBrCl	64	25.29	25.38
V	p-OCH ₃	145-6/1	1.3876	1.5929	60.18	47.77	12.41	C ₉ H ₁₂ AsOCl	69	30.38	30.42
VI	p-NO ₂	-	1.5578	1.6356	60.14	48.21	11.93	C ₈ H ₉ AsO ₂ HCl	70	28.61	28.68
VII	m-CH ₃	114/3	1.3360	1.5838	57.71	46.13	11.58	C ₉ H ₁₂ AsCl	58	32.47	32.53
VIII	m-Cl	158/2	1.4856	1.6027	58.00	46.37	11.63	C ₈ H ₉ AsCl ₂	71	29.76	29.88
IX	m-Br	162/2	1.6984	1.6174	60.91	49.27	11.64	C ₈ H ₉ AsBrCl	64	25.31	25.38
X	m-OCH ₃	148-50/3	1.3873	1.5884	59.82	47.77	12.05	C ₉ H ₁₂ AsOHCl	60	30.34	30.42
XI	m-NO ₂	-	1.5212	1.6053	59.03	48.21	10.82	C ₈ H ₉ AsO ₂ HCl	67	28.52	28.68
XII	o-CH ₃	116/0	1.3460	1.5881	57.62	46.13	11.50	C ₉ H ₁₂ AsCl	62	32.46	32.53
XIII	o-Cl	149-50/3	1.4829	1.6036	58.17	46.37	11.80	C ₈ H ₉ AsCl	73	29.77	29.88
XIV	o-Br	139/1	1.6961	1.6177	61.03	49.27	11.76	C ₈ H ₉ AsBrCl	68	25.29	25.38
XV	o-OCH ₃	145-6/3	1.3975	1.5910	59.59	47.77	11.82	C ₉ H ₁₂ AsOCl	74	30.33	30.42
XVI	o-NO ₂	-	1.5563	1.6358	60.20	48.21	11.99	C ₈ H ₉ AsO ₂ NCl	68	28.57	28.68

Secondary arsinghalides actively interact with many reagents to form more complex compounds, acting as an intermediate.

One of the most significant is the synthesis of trivalent arsenic derivatives - tertiary arsines, in which arsenic can be in both homo- and hetero-coordination states. The latter compounds are an interesting object for studying stereochemical properties.

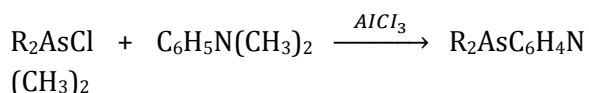
The following method for the synthesis of chiral arsines [11] is based on the ability of arsonium salts to alkylate triphenylphosphine:



The reaction proceeds under mild environment of dimethylformamide (DMF). The yields of tertiary arsines are close to quantitative.

Tertiary arsines were obtained in a sufficiently high yield using the reaction of secondary chloroarsines with aromatic hydrocarbons in the presence of aluminum chloride [12]. The presence of an aromatic

compound in the nucleus of electron-donor groups facilitates the reaction.



Tertiary arsines with double carbon-carbon bonds are synthesized [13] by direct interaction of acetylene derivatives with secondary arsinghalides under UV irradiation:



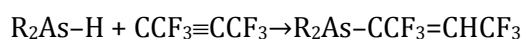
Tertiary arsines are obtained by adding secondary arsines to chlorine and fluorine-containing unsaturated hydrocarbons [14]. The reaction products are formed in high yield.



It was shown [15] that secondary arsines, due to the mobility of hydrogen, are well attached in the presence of bases to acrylonitrile with the formation of the corresponding chiral arsinonitriles:



The reaction of the attachment of secondary arsines to acetylenic hydrocarbons is given in [13]. The reaction is shown to proceed easily with the formation of tertiary ethylene derivatives of arsenic:

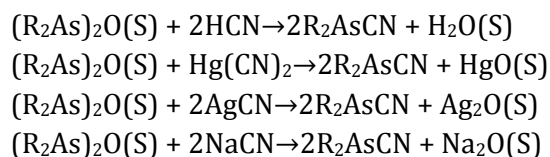


Asymmetric arsines were obtained [16] by a similar reaction of secondary arsinghalides with ethylene and acetylenic hydrocarbons under prolonged heating at 180°C.



Asymmetric As (III) derivatives containing a nitrile group are interesting subjects for studying stereochemical properties. The hydrolysis of arsinonitriles leads to the formation of the corresponding carboxy derivatives of arsenic. The synthesis of tertiary arsines with a nitrile group directly attached to the As atom was carried out by the

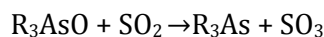
interaction of secondary arsine oxides with hydrocyanic acid, cyanides of mercury, silver, and alkaline metals [17].



The same compounds can be obtained in high yield from secondary arsinghalides too.

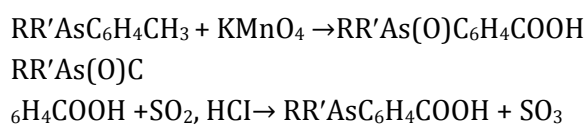
One of the most convenient methods for obtaining tertiary arsines is the reduction of their oxides [18]. This is how aliphatic, aromatic, and mixed arsines are obtained.

The reduction of oxides of three-coordinated arsenic containing three different hydrocarbon radicals leads to the formation of chiral arsines. This reaction proceeds in an acidic environment. Sulfurous anhydride and tin are most often used as reducing reagents, and hydrochloric and phosphoric acids are used as a medium.



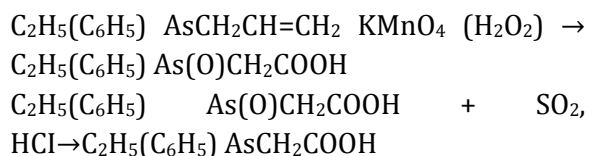
Target product yields are close to quantitative aspect. An alcoholic solution of iodine or a solution of potassium iodide is used as a catalyst in the reduction of arsine oxides with sulfurous anhydride in a hydrochloric acid environment.

The cleavage of racemic arsines using optically active components proceeds with the use of functionally substituted organo-arsenic compounds, for example, arsenic acids or amines. The synthesis of asymmetric arsines of type $\text{RR}'\text{AsC}_6\text{H}_4\text{COOH}$ was carried out [19] by oxidation of the corresponding tolylarsines with an aqueous solution of KMnO_4 , followed by treatment with sulfur dioxide in a hydrochloric acid medium:

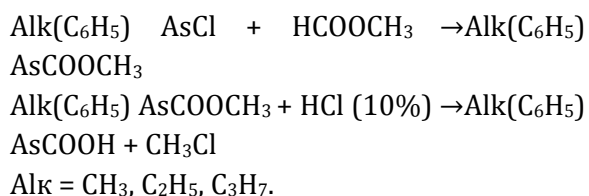


Ethylphenylarsineacetic acid was obtained by oxidation of ethylphenylallarsine (III) with a solution of KMnO_4 and 26% H_2O_2 followed by

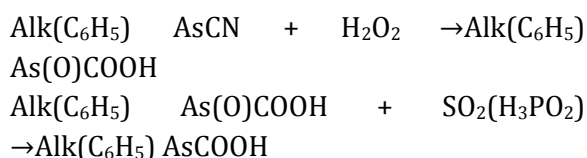
reduction. This produces several by-products; however, the target substance is obtained in high yield.



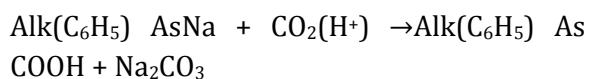
Ethyl phenylarsineacetic acid was isolated from the reaction mixture of by-products by repeated distillation in a vacuum. Alkylarylarsineformic acids were obtained [20] by hydrolysis of the corresponding esters, nitriles, as well as by carbonization of sodium arsinides.



Hydrolysis of methyl ester of ethylphenylarsineformic acid with 10% HCl solution leads to the formation of a mixture of arsinghalide and ethidphenylarsineformic acid. Alkylarylarsineformic acid was obtained by hydrolysis of alkylarylarsinonitrile with hydrogen pyroxide in high yield.



During the carbonation of sodium arsinides, the corresponding arsynamoic acids were obtained with a 75% yield.



Synthesis of ethyl-o-tolylarsine chloride (XII)

Following all the requirements of safety regulations (tetraethyl lead, as well as the starting arylarsine dichlorides and their vapors have the strongest toxic effects), we placed 94 g of o-tolylarsine dichloride into a round-bottom flask equipped with a

mechanical stirrer, reflux condenser, thermometer, and we carefully added dropwise dropping funnel, heated in an oil bath to 110°C and 42 g of tetraethyl lead. Cloudiness of the reaction mixture, the formation of a white precipitate and a sharp rise in temperature indicate the progress of the reaction. During the synthesis, overheating of the reaction mixture should not be allowed, as this leads to a decrease in the product yield. After adding all the tetraethyl lead, the reaction mixture was heated at the same temperature for another hour. Distillation in vacuum produced 78 g (86%) of ethyl-o-tolylarsine chloride, b.t. 125°C (P 5mm Hg), n_{D}^{20} 1.5881, d_4^{20} 1.3467.

Arsenic content, %: As 32.23 was found. $\text{C}_9\text{H}_{12}\text{AsCl}$. As 32.53 was calculated. The IR spectrum of ethyl-o-tolylarsine chloride contains characteristic absorption bands in: ν_s and ν_{as} AsC_2H_5 - 2850-2980; δ_s and δ_{as} AsC_2H_5 - 1380- 1460 cm^{-1} ; ν As - C ethyl- 563-565 cm^{-1} ; ν Ph - As 1080 cm^{-1} ; δ Ph - As 490 cm^{-1} . The PMR spectrum contains C_6H_4 - 7.12-7.63; Ph - CH_3 - 2.42; CH_2 -2.07, CH_3 - 1.23 δ ppm. IR spectra of the studied compounds were obtained on an UR-20 spectrophotometer using a KBr prism in the range of 400-700 cm^{-1} , NaCl in the range of 700-1800 cm^{-1} , and LiF in the range of 1800=3800 cm^{-1} , in vaseline oil between two KBr plates. The thickness of the investigated layer was $d=0.43$ mm. PMR spectra were recorded on Varian T-60 (60 mgc) in carbon tetrachloride, internal tetramethylsilane standard (TMS).

Ethylphenyl-, -o-, -m-, -p-tolyl-, anisyl-, chloro-, bromo-, nitrophenylarsine chlorides were obtained in a similar way.

Conclusion

The authors have reviewed the literature data on the synthesis of secondary alkylaryl-, diarylarsinghalides and their reactivity. A preparative method for the synthesis of chiral ethyl arylarsine chlorides using tetraethyl lead

as an ethylating reagent has been tested and recommended.

The authors are confident that the data described in this work will fill a niche in the technology for the synthesis of arsenic derivatives and will be useful in studying the chemistry of organoarsenic compounds.

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