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Methods for the synthesis of arsines and arsine dihalides

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ABSTRACT

Arsenic is an essential biologically active element, and its compounds are used in various fields and areas of activity. Arsenic chemistry is widely used in agriculture, industry, and medicine. Many organic arsenic compounds have bactericidal and herbicidal properties necessary for practical use; some of them found its application in polymer chemistry. This necessitates the production of new substances with previously known properties. Therefore, the problem of studying methods for the synthesis of organic arsenic compounds is important and relevant. The present article is devoted to the analysis of methods for the synthesis of primary arsines and the corresponding arsine dihalides. Based on a study of literature containing a description of various methods for preparing compounds of this group, as well as on the basis of the results of own experimental studies, the author makes a choice in favor of the synthesis of primary aryl arsine dihalides by reduction of the corresponding arsonic acids. Subsequent substitution of halogen atoms can produce compounds of a specific structure. Thus, using aryl arsonic acids as starting products for the synthesis of subsequent classes of organic arsenic compounds, it is possible to obtain organic arsenic compounds of a given structure and complexity. A detailed description of the methods of conducting experiments is made, their comparative characteristics are given, and the physical properties of the obtained substances are described.

KEYWORDS: organic arsenic compounds, arsines, arsine dihalides, aryl arsonic acids, arsine oxide.

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Métodos para la síntesis de arsinas y dihaluros de arsina

RESUMEN

El arsénico es un elemento biológicamente esencial, y sus compuestos se utilizan en diversos campos y áreas de actividad. La química del arsénico se usa ampliamente en la agricultura, la industria y la medicina. Muchos compuestos orgánicos de arsénico tienen propiedades bactericidas y herbicidas necesarias para su uso práctico; algunos de ellos encontraron su aplicación en la química de polímeros. Esto requiere la producción de nuevas sustancias con propiedades previamente conocidas. Por lo tanto, el problema de estudiar métodos para la síntesis de compuestos de arsénico orgánico es importante y relevante. El presente artículo está dedicado al análisis de métodos para la síntesis de arsinas primarias y los correspondientes dihaluros de arsina. Basado en un estudio de literatura que contiene una descripción de varios métodos para preparar compuestos de este grupo, así como en base a los resultados de estudios experimentales propios, el autor toma una decisión a favor de la síntesis de dihaluros de aril arsina primaria por reducción de los correspondientes ácidos arsónicos. La posterior sustitución de átomos de halógeno puede producir compuestos de una estructura específica. Por lo tanto, utilizando ácidos aril arsónicos como productos de partida para la síntesis de clases subsiguientes de compuestos de arsénico orgánico, es posible obtener compuestos de arsénico orgánico de una estructura y complejidad dada. Se realiza una descripción detallada de los métodos para realizar experimentos, se dan sus características comparativas y se describen las propiedades físicas de las sustancias obtenidas.

PALABRAS CLAVE: compuestos orgánicos de arsénico, arsinas, dihaluros de arsina, ácidos aril arsónicos, óxido de arsina

Introduction

The subject of the work is relevant and important because many arsenic compounds are of interest for solving highly significant scientific and practical problems in various fields of life.

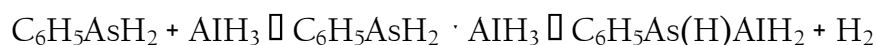
The objective of this work is to study, compare, and select the most effective way to obtain organic arsenic compounds of a given structure. Objects of research are arsines and arsine halides and methods for their synthesis.

1. Methods

Primary arsines $RAsH_2$, used for the synthesis of secondary and tertiary arsines, are usually obtained by reduction of the corresponding acids, their salts (Feltham et al., 1967; Cookson and Mann, 1949), arsine halides (Brooker et al., 1958; Abbers et al., 1952), arsenic

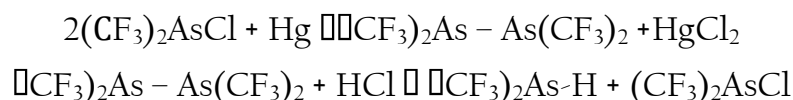
compounds containing the As=As bond, and oxides (Tzschach and Lange, 1964). The most effective reducing agents are zinc dust and hydrochloric acid (Feltham, 1967; Brooker et al., 1958; Newbery and Philips, 1928), zinc amalgam (Pabmer and Dehn, 1901; Tzschach and Lange, 1964; Rapoport and Iliinskaia, 1963), zinc copper (Wigren, 1930), and zinc platinum (Abbers et al., 1952). Depending on the nature of the reducing agent, the reaction does not always proceed with a good yield. For example, in (Cragoe et al., 1947) methylphenylchlorarsine was reduced to the corresponding arsine with zinc amalgam in methanol with a good yield, while the reduction of dialkylchlorarsines with LiAlH₄ did not give satisfactory results in (Issleib and Tzschach, 1961; Stone and Burg, 1954).

To reduce CF₃AsJ₂ and (CF₃)₂As-As(CF₃)₂, the researchers used LiAlH₄, hydrochloric acid, and copper-coated zinc (Emeleus et al., 1953). When phenyl and diphenylarsine chlorides were reduced with lithium aluminum hydride and borohydride, the corresponding arsines were obtained in high (81%) yield (Kockel, 1956; Cullen, 1961). The restoring effect of LiAlH₄ is not always effective because it is assumed to interact with the resulting arsine according to the following scheme:



For recovery under these conditions, both C₆H₅AsCl₄ and C₆H₅AsCl₂ can be used. The final reaction product in both cases will be C₆H₅AsH₂.

During the reduction of (CF₃)₂AsCl with metallic mercury in hydrochloric acid, the formation of diarsine is supposed, which under the action of HCl is decomposed by the As-As bond:

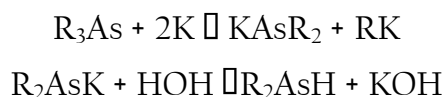


According to the authors of (Cavell and Dobbil, 1967; Fichter and Elkind, 1916), the reduction of the corresponding arsiniodides with mercury in hydrochloric acid ensures more effective results. Thus, (CF₃)₂AsJ, J₂(CF₃)₂As-As(CF₃)₂J₂ and (CF₃)₂AsJ₃ are reduced. As a result, (CF₃)₂AsH was obtained in high yield.

Primary and secondary arsines can be obtained through metal arsinides formed by the interaction of AsH_3 with active metals such as Na, K, or Ca in liquid ammonia. The reaction of the corresponding metal arsinides with alkyl or aryl halides leads to the formation of primary and secondary arsines (Johnson and Pechwkas, 1937; Tzschach and Pacholke, 1964):



The reaction of calcium diarsinide $\text{Ca}(\text{AsH}_2)_2$ with methyl chloride forms a mixture of products consisting of methyl, dimethyl, and trimethylarsines. Secondary dialkyl or mixed alkylarylsarsines can be prepared by heating triaryl and alkyl diarylsarsines with potassium metal in dioxane. Hydrolysis of the resulting potassium arsinide with water leads to the synthesis of secondary arsine in high yield (Issleib and Tzschach, 1961; Tzschach and Lange, 1964).



Magnesium arsinides react similarly with water (Blicke and Oneto, 1935).

To obtain primary arsenic aryl dihalides, the reaction of arsenic trichloride with organometallic compounds is most often used. However, it should be emphasized that the use of organic magnesium reagents in this reaction is ineffective due to their interaction with arsenic trihalides with the simultaneous substitution of all halogen atoms (Freidlina, 1945).

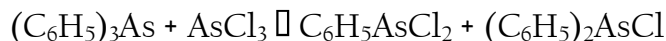


The reaction of aromatic organic mercury compounds with arsenic trichloride is mainly used to produce aryl arsine dichlorides. In this reaction, an excess of arsenic trichloride and an increase in the reaction temperature to 200–230 °C make it possible to obtain only aryl arsine dichlorides, in good yield.



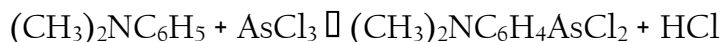
Monoaryl arsine dichlorides are also obtained by the reaction of arsenic trichloride with aromatic organic mercury salts (Michaelis, 1894). Secondary and tertiary arylarsines formed during this reaction are disproportionate under the action of the resulting mercuric chloride and improve the yield of arylarsindichlorides.

In addition to those considered, one of the most convenient methods for obtaining primary aromatic arsenic dihalides is the reaction of triaryarsines with arsenic trihalides (Michaelis and Reese, 1882).



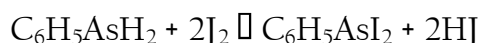
The disproportionation reaction of tertiary arsines that have aryl radicals under the action of arsenic trichloride leads to the formation of the corresponding primary arylarsine dihalides. This reaction is carried out by prolonged heating of the mixture. The yield of primary arylarsine dihalides depends on the ratio of reagents and increases when excess arsenic trichloride is used.

The primary aromatic arsine dihalides in the product mixture are obtained by the interaction of aromatic hydrocarbons with arsenic trichloride.



The presence of electron-donating substituents in the benzene ring increases the yield of the main products (Cullen, 1966).

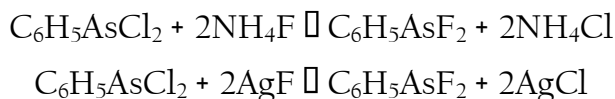
Primary arylarsine dihalides can be synthesized from the corresponding arsenic hydrides by reacting with halogens, hydrogen halides and inorganic metal and phosphorus halides. According to this technique, arylarsine dichloride was obtained by the interaction of phenylarsine with chlorides of mercury, tin, phosphorus, arsenic, and antimony (Kamai and Gatilov, 1961):



Primarily substituted arylarsine dihalides can be obtained from the corresponding oxides, which easily react with hydrogen halides (Michaelis and Schulte, 1982):



Primary arylarsine difluorides are obtained by this reaction using hydrofluoric acid. However, as described by the authors of (Lang et al., 1946), the best method for producing fluorine derivatives is the exchange interaction of arylarsine dichloride with ammonium or silver fluorides.



The considered methods for the preparation of primary arylarsine dihalides are much inferior to the method consisting in the reduction of arylarsonic acids in the presence of hydrogen halide:



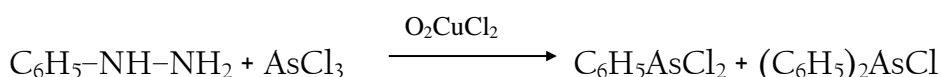
Reducing agents in this reaction are sulfur dioxide, hypophosphorous acid, phosphorus trichloride, sodium hypophosphate, thionyl chloride, and other reducing agents. The reduction reaction is catalyzed by iodide ion and is usually carried out in concentrated hydrochloric acid.

The reduction of arylarsonic acids with sulfur dioxide in the presence of other HX acids (X= Br, J) leads to the production of bromine and iodarsines (Freidlina, 1945).

Primary arylarsine halides can be obtained from aryl diarsine halides. According to this method, Michaelis obtained phenylarsine diiodide by oxidation of phenylarsenic diiodide with oxygen in an aqueous medium:

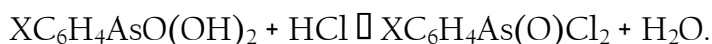


The authors of (Brooker and Nikiforova, 1958) proposed a method for the preparation of primary aryldiarsine halides by the interaction of phenylhydrazine with arsenic trichloride in the presence of copper chloride and oxygen.

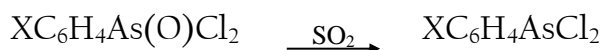


2. Results and discussion

Arylarsine dichlorides were synthesized by us by reduction of arylarsonic acids with sulfur dioxide in a concentrated hydrochloric acid (Yambushev et al., 1983). The recovery process proceeds in two stages. In the first, as arylarsonic acid dissolves in hydrochloric acid, the hydroxyl groups associated with the arsenic atom are exchanged for chlorine atoms to form arsenic acid chlorides in a hydrochloric acid solution.



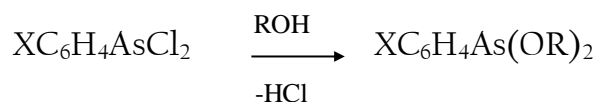
At the second stage, when acting with sulfur dioxide, the acid chlorides are reduced to the corresponding aryl aromatic dichlorides:





Some physical constants and analytical data on the obtained monosubstituted arylarsine dichlorides are given in Table 1.

Arylarsine dichlorides $XC_6H_4AsCl_2$, $X = o-, m-, p-H, CH_3, OCH_3, NO_2, n-J, CH_3$ are crystalline substances with a low melting point. Compounds of $o-H, CH_3, m-CH_3, m-, n-CH_3O, Cl, Br$ - liquids that are well distilled in a vacuum, have a characteristic arsenic trichloride odor, dissolve well in both polar and non-polar solvents, and are quite stable during storage. However, water and other solvents with active hydrogen atoms, when heated, can start interaction:



Phenylarsine dichloride (Los K. Synthetic poisons, 1963), which is part of the group of chemical warfare agents, as well as its synthesized derivatives, discussed in this section, have a pronounced skin-blistering effect.

The experimentally found and calculated values of the elemental analysis of arsenic, as well as the molecular refraction data of the synthesized arylarsine dichlorides, confirm their compliance with the accepted structures. The found data of atomic refraction to arsenic averaged 11.63 for these compounds, which is also within the normal range and complies with literature data.

Table 1

Arylarsindichlorides $XC_6H_4AsCl_2$

№	X	B. t., °C - p, mmHg	M.t. , °C	d_4^{20}	n_D^{20}	MR _D		AR _D , As	Out put %	As, %	
						found	calculated			found	calculated
I	p-H	112- 13/2	-	1.650 4	1.637 1	38.4 9	37.14	11.35	68	33.17	33.63
II	p- CH ₃	-	40	-	-	-	-	-	72	31.29	31.64
III	p-Cl	112- 23/1	-	1.747 6	1.64 91	53.6 7	42.00	11.67	84	28.9 7	29.12

IV	p-Br	143- 44/2	33	1.997 5	1.674 1	56.7 3	44.90	11.63	73	24.6 5	24.83
V	p- OCH ₃	140- 41/1	-	1.676 4	1.669 5	56.3 3	43.40	12.93	62	29.17	29.64
VI	p-I	-	41	-	-	-	-	-	56	21.09	21.48
VII	p- NO ₂	128/2	30	1.56 40	1.621 7	-	-	-	61	27.5 4	27.98
VII I	m- CH ₃	128/2	-	1.56 40	1.621 7	53.3 4	41.76	11.53	74	31.17	31.64
IX	m-Cl	128/2	-	1.758 2	1.64 43	53.0 4	42.00	11.04	76	29.0 5	29.22
X	m-Br	187/4	-	2.00 79	1.667 8	56.0 3	44.90	11.13	70	24.5 7	24.83
XI	m- OCH ₃	135- 36/1	-	1.626 4	1.630 0	55.3 4	43.40	11.94	69	29.31	29.64
XII	m- NO ₂	-	51	-	-	-	-	-	77	27.7 9	27.98
XII I	o- CH ₃	91- 93/2	-	1.58 40	1.629 8	53.2 2	41.76	11.46	81	31.25	31.64
XI V	o-Cl	156- 57/2	44	1.773 2	1.641 3	52.3 9	42.00	11.39	80	2.02 9	29.12
XV	o-Br	-	-	-	-	-	-	-	66	24.3 5	24.83
XV I	o- OCH ₃	-	-	-	-	-	-	-	75	29.2 9	29.64
XV II	o- NO ₂	-	-	-	-	-	-	-	64	27.6 3	27.98

o-tolylarsine dichloride synthesis.

A hydrochloric acid solution of o-tolylarsonic acid was placed in a 2L round bottom flask equipped with a reflux condenser. A 10% alcohol solution of iodine was added. The reaction mixture was heated to a boil in a water bath and, maintaining this temperature, a strong stream of sulfur dioxide was applied. After the recovery process was completed, the aqueous layer was drained, the product was extracted with benzene. The resulting solution was filtered, the solvent was distilled off, and the residue was distilled in vacuum. 98g (96%) of the product were isolated. B.t. 93°C (1mm Hg); n_D^{20} 1.6298; d_4^{20} 1.5846 (gradually crystallizes, M.t. 41°C).

Arsenic content, %: Found As 31.44 C₇H₇AsCl₂. Calculated As 31.64. IR o-tolylarsine dichloride contains all the main absorption bands characteristic of the aromatic ring in the

region of 7 As-Ph 1070-1130; δ Ph - As 485 cm^{-1} . RS contains in the region of 360-395 cm^{-1} very strong bands characteristic of ν_{as} and ν_{s} AsCl_2 vibrations. PMR contains resonant signals of aromatic protons at δ 7.11-7.83, methyl group at δ 2.45 m.d. regarding TMS.

Using a similar technique, phenyl-*o*-, *m*-, *p*-tolyl-, anisyl-, chloro-, bromo-, nitrophenylarsine dichlorides (I-XVII) were obtained, some physical constants and analytical data of which are given in Table 1.

Summary

The chemistry of organic arsenic compounds has many methods developed to obtain organic arsenic derivatives of various classes. An analytical review of the synthesis of primary arsines and the corresponding arsine dihalides was carried out in the work, their negative and positive points were analyzed. The most effective method has been tested and recommended.

Conclusions

The intensive development of the chemistry of organic element compounds, including in the field of the study of derivatives of the fifth group, poses new challenges. The author expresses confidence that in choosing a research strategy for organic arsenic compounds, this work will serve as a major asset for chemists.

Acknowledgments

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