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Organometallic reactions of secondary arsingalogenides

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The experimental possibility of splitting asymmetric derivatives of three-and four-coordinated arsenic into optically active antipodes had for a long time remained unattainable for many well-known chemists, including Meisenheimer (Germany), Kamai (Russia), etc. When a racemic mixture of chiral arsines is cleaved with optically active components, a functional group (acidic or basic) is used that is contained in one of the fragments bound to the arsenic atom. Chiral arsines containing a carboxyl group are synthesized by oxidation of the corresponding fragments. Based on the results, to develop effective methods for the synthesis of tertiary arsines containing functional groups $XC_6H_4(C_2H_5)AsC_6H_4У$, where У=o-, m-, p-NH_2, COOH, the reactivity of ethylarylarsine chlorides with organometallic compounds should be considered.

KEYWORDS

Alkyldiarylarsines; ethylarylarsine chlorides; asymmetric; secondary; tertiary arsines; carboxyphenylarsines; chiral arsines.

Introduction

Functional groups are part of organic molecules that have the characteristic properties of a particular molecule. Some examples of these functional groups include alcohols, carboxylic acid groups, amine groups, and so on. These functional groups are the side groups of the main carbon chain. In other word, functional groups are part of a large molecule. It can be an atom, a group of atoms or even an ion. Most of the time, these groups are responsible for the reactions that the molecule may undergo. These functional groups must be considered when naming any organic molecule. An application group always has space in its structure to be able to attach to the carbon chain. The main difference between alkyl and aryl is that the alkyl group has no aromatic ring, while the aryl group has one aromatic ring.

An alkyl group is a functional group found in organic molecules. It is an alkane with a hydrogen atom that is missing from its chain. This empty point can be attached to the carbon atom of the carbon chain. This alkyl group can be a simple chain, branched or cyclic, but it does not have aromatic rings. Alkyl groups contain only carbon and hydrogen atoms in their structure. The general formula of an alkyl group can be expressed as CnH2n + 1, which differs from the formula of an alkane, CnH2n + 2, by the loss of a hydrogen atom. Thus, alkyl groups are derived from alkanes. The smallest alkyl group is the methyl group, which can be as -CH3. derived from methane alkane (CH4). Cycloxyl groups are sometimes confused with aromatic groups. But there is a big difference between them. Cycloclans are saturated and have no double bonds, but aromatic rings are unsaturated and have double bonds in their structure (e.g., cyclohexane). The word

saturation indicates that it has the largest number of hydrogen atoms to which it can bond. Even in morphology, cycloclans are three-dimensional structures while aromatic compounds are flat structures. Hence, all alkyl groups are saturated because alkyl groups are derived from alkanes.

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 organoarsenic compounds. Such studies are of great theoretical and practical interest.

The reactivity of secondary arsinghalides in the interaction with organic metal compounds has been studied quite well. The most commonly used are the reactions of secondary organo-arsenic halides with organic derivatives of active metals. However, some organometallic compounds have now lost their preparative value and are used less frequently. This primarily concerns organozinc and organomercury compounds, which are replaced by lithium, sodium, potassium compounds, and Grignard reagents.

Methods

The research methods of arsenic arylation using organometallic compounds included methods of oxidizing of a methyl group to a carboxyl group; method of carboxylation and reduction of carboxyphenylarsine oxides with sulfur dioxide; and spectroscopic methods.

Results and discussion

The reaction of secondary ethylarylarsinehalides with Grignard reagents proceeds with the formation of tertiary arsines. Therefore, for the synthesis of tertiary arsines that do not contain functional substituents in the benzene ring, we have chosen the simplest and experimentally effective method based on the interaction of arylmagnesium halides with the corresponding ethylarylarsine chlorides [1,2].

$XC_6H_4As(C_2H_5)\,Cl + BrMgC_6H_4У \rightarrow XC_6H_4(C_2H_5)\,AsC_6H_4У$

This smoothly proceeding reaction complicates the interaction of secondary ethylarylarsine chlorides with arylmagnesium halides containing strong electron-donating substituents in the benzene ring. For example, as a result of the interaction of ethylarylarsine chlorides with N, N - dimethylaminophenylmagnesium bromide in tetrahydrofuran, the corresponding tertiary arsines were obtained in a low yield, which agrees with the results of [3]. A higher yield of this product (73%) was obtained by our organolithium method described below.

The physicochemical characteristics of tertiary ethyldiarylarsines (I-XVII) obtained by our organomagnesium method are given in Table 1.

Among them, $XC_6H_4(C_2H_5)\,AsC_6H_4У$, where X = o-, m-, p-Cl, CH_3O, o-, m-Br, Y= H, Cl, Br, were obtained and characterized for the first time.

The synthesized tertiary ethyldiarylarsines are colorless or slightly yellowish viscous liquids with high boiling points and distilled in vacuum without decomposition. All of them have a characteristic odor, dissolve well in many organic solvents and are stable when stored under normal conditions.

The experimentally found and calculated values of elemental analysis for arsenic, as well as the data of atomic and molecular refractions, confirm their compliance with the accepted structures.

TABLE 1 Physical characteristics of ethylaryl-p-tolylarsines $XC_6H_4(C_2H_5)$ $AsC_6H_4CH_3$-p (I-XIV) and $XC_6H_4(C_2H_5)$ $AsC_6H_4У$-p (XV-XVII) (У=H, CI, Br)

№	X	T.boil.,°C (P, mmHg)	d_4^{20}	n_D^{20}	mr_d		AR_D, As	Formula	Output %	As, %	
					found	calculated				found	calculated
I	H	230/6	1.2098	1.6123	78.21	65.36	12.85	$C_{15}H_{17}As$	83	27.41	27.52
II	p - CH_3	238/2	1.1937	1.6072	82.75	69.97	12.78	$C_{16}H_{19}As$	71	26.03	26.17
III	p - CI	219/2	1.2934	1.6169	82.57	70.23	12.33	$C_{15}H_{16}AsCI$	68	24.27	24.43
IV	p - Br	255/2	1.4655	1.6338	85.62	73.13	12.49	$C_{15}H_{16}AsBr$	73	21.21	21.33
V	p - OCH_3	240/3	1.2390	1.6113	84.62	71.61	13.01	$C_{16}H_{19}As0$	64	24.68	24.78
VI	p - $N(CH_3)_2$	261/1	1.1999	1.6271	93.03	78.54	14.49	$C_{17}H_{22}As$	63	23.69	23.80
VII	m - CH_3	242/2	1.2392	1.6323	82.34	69.97	12.37	$C_{16}H_{19}As$	57	26.02	26.17
VIII	m - CI	204/2	1.3005	1.6154	82.27	70.23	12.04	$C_{15}H_{16}AsCI$	59	24.36	24.43
IX	m - Br	228/2	1.4621	1.6349	85.91	73.13	12.00	$C_{15}H_{16}AsBr$	64	21.30	21.33
X	m - OCH_3	287/3	1.2469	1.6319	86.99	71.61	13.74	$C_{16}H_{16}As0$	59	24.71	24.78
XI	o - CH_3	74(T.mel.)	—	—	—	—	—	$C_{16}H_{19}As$	67	26.08	26.17
XII	o - CI	194/1	1.3067	1.6230	82.72	70.23	12.49	$C_{15}H_{16}AsCI$	65	24.31	24.43
XIII	o - Br	238/2	1.4711	1.6363	85.56	73.13	12.42	$C_{15}H_{16}AsBr$	58	21.29	21.33
XIV	o - OCH_3	234/2	1.2790	1.6151	82.40	71.61	10.79	$C_{16}H_{19}As0$	74	24.72	24.78
XV	H	234/1	1.3190	1.6260	69.22	60.74	8.50	$C_{14}H_{15}As$	63	28.07	29.06
XVI	p - CI	240/5	1.3942	1.6282	83.23	70.48	12.75	$C_{14}H_{13}AsCI_2$	57	21.79	22.93
XVII	p - Br	—	—	—	—	—	—	$C_{14}H_{13}Br_2$	77	33.87	34.78

The reaction of secondary ethylarylarsine chlorides with arylmagnesium halides proceeds uniformLy in the case of using arylmagnesium bromides that do not contain two halogen atoms in the benzene ring and functional groups that simultaneously react with magnesium, or that strengthen the chemical bond between the halogen and the carbon atom of the benzene ring. The corresponding carboxylated arsines [4,5] were synthesized from tertiary chiral arsines by oxidation of the methyl group of the tolyl radical bound to the arsenic atom with a solution of $KMnO_4$ followed by the reduction of the reaction products with sulfur dioxide in a hydrochloric acid medium. The reaction proceeds in two stages. In the first stage, the products of oxidation are alkylarylcarboxyphenylarsioxides, which, as reduced in the second stage, produce alkylarylcarboxyphenylarsines.

$XC_6H_4(C_2H_5)$ As-$C_6H_4CH_3$ + $KMnO_4$ (SO_2, HCI) →$XC_6H_4(C_2H_5)$ As–C_6H_4COOH
X= o-, m-, p-H, Br.

This method provided a number of asymmetric alkylarylcarboxyphenylarsines [6-10]. As a result of the experiments, we found a number of disadvantages of this method. First, it includes several laborious steps, for example, for the synthesis of the corresponding chiral alkylaryl tolylarsines and the oxidation of the latter to carboxy derivatives; secondly, this method involves the use of scarce and expensive aryl halides. In this regard, it can be applied only in exceptional cases, such as to obtain individual compounds, the synthesis of which by other methods fails.

The above oxidation method cannot be used to obtain analogous compounds containing substituents unstable to oxidation, such as CH_3 and CH_3O, in the second benzene ring, as it leads to the simultaneous oxidation of the substituents of both benzene rings with the formation of the corresponding oxidation products. Accordingly, we have developed a procedure for the preparation of the discussed compounds, which consists in the carboxylation of the corresponding chiral

ztylarylarsinephenylylmagnesium bromides with carbon dioxide to tetrahydrofuran.

$XC_6H_4(C_2H_5)$ As-$C_6H_4Br+Mg\rightarrow$
$XC_6H_4(C_2H_5)$ As-$C_6H_4MgBr+CO_2\rightarrow$
$XC_6H_4(C_2H_5)$ As-C_6H_4COOH
X= o-, m-, p-CH_3, OCH_3.

In organic chemistry, the specified method for the synthesis of carboxylic acids is known [11]; however, we used it for the first time in the synthesis of organo arsenic compounds. Another our method used in this study for the synthesis of chiral carboxyphenylarsines is based on the ability of the corresponding secondary ethylcarboxyphenylarsine chlorides to react with aryl halides under the action of sodium. This reaction is considered in detail below using the example of the interaction of secondary arsine chlorides with bromanilines.

$HOOCC_6H_4(C_2H_5)$ As–CI+3Na+$BrC_6H_4X\rightarrow$
$XC_6H_4(C_2H_5)$ As-$C_6H_4COONa+HCI\rightarrow$
$XC_6H_4(C_2H_5)$ As-C_6H_4COOH
X= o-, m-, p-CH_3, OCH_3.

Our proposed magnesium-and sodium-organic methods [12] for the synthesis of chiral carboxy derivatives of arsines are more effective than the known oxidation method and provide a higher yield of the target products, from 43% to 78% (see Table 2)

TABLE 2 Physical characteristics of ethylarylcarboxyphenylarsines R (R′) AsC_6H_4COOH (I-XVII)

№	R	R′	Output %	T. melt., °C	As,% found	As,% calculated	Formula	M
I	CH_3	C_6H_5	72	144	25.85	25.99	$C_{14}H_{13}AsO_2$	288.18
II	C_2H_5	C_6H_5	70	116	24.60	24.79	$C_{15}H_{15}AsO_2$	302.21
III	C_2H_5	CI	72	80	28.54	28.75	$C_9H_{10}O_2AsCI$	260.56
IV	C_2H_5	$C_{12}H_9$	68	143	19.59	19.80	$C_{21}H_{19}AsO_2$	378.31
V	C_2H_5	CI	70	105	28.62	28.75	$C_9H_{10}O_2AsCI$	260.56
VI	C_2H_5	C_6H_5	66	112	24.52	24.79	$C_{15}H_{15}AsO_2$	302.21
VII	C_2H_5	C_6H_5	30	109	24.49	24.79	$C_{15}H_{15}AsO_2$	302.21
VIII	C_2H_5	o-BrC_6H_4	78	82	19.65	19.65	$C_{15}H_{14}O_2AsBr$	381.12
IX	C_2H_5	m-BrC_6H_4	63.1	124	19.61	19.65	$C_{15}H_{14}O_2AsBr$	381.12
X	C_2H_5	p-BrC_6H_4	73	109	19.64	19.65	$C_{15}H_{14}O_2AsBr$	381.12
XI	C_2H_5	o-CIC_6H_4	52.7	108	22.14	22.25	$C_{15}H_{14}O_2AsCI$	336.65
XII	C_2H_5	m-CIC_6H_4	71.4	102	22.21	22.25	$C_{15}H_{14}O_2AsCI$	336.65
XIII	C_2H_5	p-CIC_6H_4	62	109	22.17	22.25	$C_{15}H_{14}O_2AsCI$	336.65
XIV	C_2H_5	p-$N(CH_3)_2$	56	71	19.59	19.68	$C_{17}H_{20}O_2AsNCI$	380.73
XV	C_2H_5	p-$N(CH_3)_2HCI$	65	75	17.87	17.96	$C_{17}H_{21}O_2AsNCI_2$	417.19
XVI	C_2H_5	p-CH_3	43	51	23.58	23.69	$C_{16}H_{17}O_2As$	316.24
XVII	C_2H_5	p-CH_3O	57	53	22.47	22.55	$C_{16}H_{17}O_3As$	332.24

Synthesis of tertiary ethyl diarylarsines

The solution of 54 g of ethyl phenylarsine chloride in 40 mL absolute ether was added dropwise to Grignarov's reagent made of 52.5 g of p-bromotoluene and 7.6 g of magnesium in 150 mL ether, which was obtained in a round-bottom flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. The mixture was heated for 1 hour and decomposed with an aqueous solution of ammonium chloride. The organic layer was separated, washed with water, and dried with calcium chloride. After distilling off the ether, the product was distilled under vacuum at 230° (6 mm). As a result of distillation, 43.8 g (63.5%) of the compound were isolated; n_D^{20}1.6123, d_4^{20}1.2098. Arsenic

content, %: As 27.41 was found. $C_{15}H_{17}As$. As 27.52 was calculated.

The IR spectrum of ethylphenyl-p-tolylarsine contains characteristic absorption bands as follows: VAs - C sp^2 1100-1115; VAs - C sp^3 562; V=CH 670, 3012, 3068; VCC sp^2 1330, 1392, 1432, 1495, 1581, 1566; ω CC sp^2 695; δ CH sp^2 1018, 1078, 1143, 1182, 1266; ω CH sp^2 727, 738. 800. 845. 910, 983; α C-C-C sp^2 617, 638, 1000; δ C_6H_4 471, 496; oscillations C_2H_5 from 1376 to 2996 cm^{-1}. The PMR spectrum contains signals characteristic of: C_6H_4 7.02-7.21; CH_3Ar 2.22; CH_2 192; CH_3 1.11 δ ppm.

Ethylphenyl-o-, -m-, -p-tolyl-, anisyl, chloro-, bromo-, p-tolylarsines were obtained in a similar way (Table 1, I-XIV).

Tertiary substituted chiral ethyldiarylarsines are generally colorless or slightly yellow viscous liquids with a high boiling point. They have a specific, arsine-characteristic smell, well-soluble in polar solvents, but insoluble in water and stable for storage under normal conditions. The calculated atomic refraction of arsenic 12.43 did not differ from the data known for some of them.

Synthesis of tertiary ethylarylcarboxyphenylarsines

Ethyl-o-bromophenyl-p-arboxyphenylarsine. 9.8 g of ethyl-o-bromophenyl-p-tolylarsine was added dropwise and with stirring to a two-fold excess of $KMnO_4$ (17.2 g) in 300 mL of water heated to 80°C. Heating continued for 20 hours. After completion of the reaction, excess $KMnO_4$ in the reaction mixture was reduced with isopropyl alcohol, and the manganese dioxide precipitate was separated and washed. The filtrate and washings were combined and the water was distilled off to 100 mL. Hydrochloric acid was added to the remaining solution until ethyl-o-bromophenyl-p-carboxyphenylarsine oxide was completely isolated in the form of a white or slightly greenish precipitate, and this oxide was reduced, with heating, with sulfur dioxide. The oily product formed at the bottom of the flask was crystallized. Ethyl-o-bromophenyl-p-carboxyphenylarsine recrystallized from hexane or octane is a white fine crystalline substance. 7.5 g yielded (72.8%), T.melt. 109°C. Arsenic content, %: As 19.64 was found. $C_{15}H_{14}O_2AsBr$. As 19.65 was calculated. The IR spectrum of ethylphenyl-p-tolylarsine contains characteristic absorption bands as follows: V C-H sp^2 3060-3040; V C=C 1595-1465; V OH 3300-2200; δ C-OH sp 1415, V C-O(H) 1290; V As $-C_{arom.}$ 1022; V As $-C_{alif.}$ 545 cm^{-1} Ethyl-, o-, m-, p-Br, CI-phenyl-carboxyphenylarsines (VIII-XIII), presented in Table 2, were synthesized in a similar way.

Conclusion

The authors have reviewed the literature data on the synthesis of tertiary alkyldiarylarsines and their reactivity. A method for the synthesis of chiral ethyldiarylarsines and ethylarylcarboxyphenylarsines has been tested and recommended.

The authors are confident that the data described in this work can be used for the synthesis of tertiary arsines and will be useful in the study of the chemistry of organoarsenic compounds.

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