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REACTION OF 10-METHYL(PHENYL)-5,10-DIHYDROPHENARSAZINE 10-OXIDES WITH HYDRIODIC ACID

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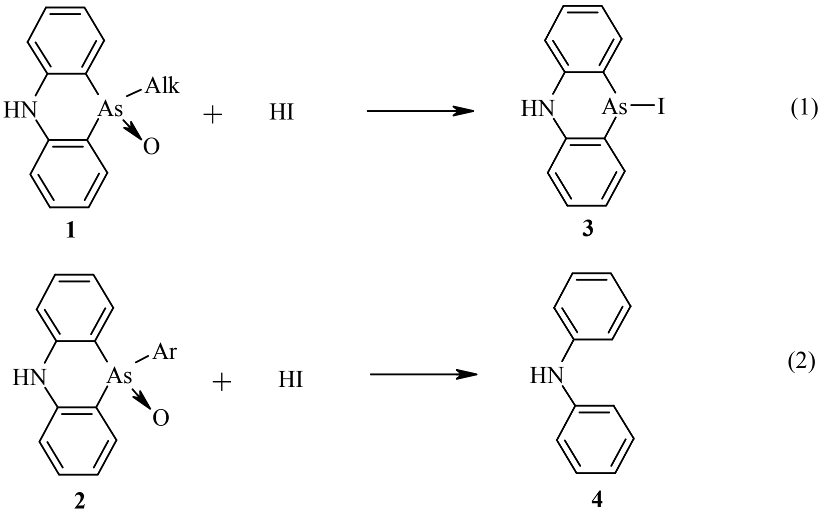
We have studied the reaction of 10-methyl(phenyl)-5,10-dihydrophenarsazine 10-oxides with hydriodic acid and we have established the structure of the products by high-resolution mass spectrometry. We have shown that when the methyl group is replaced by a phenyl group in 5,10-dihydrophenarsazine 10-oxides, cleavage of the endocyclic arsenic–carbon bonds occurs.

Keywords: hydriodic acid, 10-methyl-5,10-dihydrophenarsazine 10-oxide, 10-phenyl-5,10-dihydrophenarsazine 10-oxide, mass spectra.

When 10-alkyl-5,10-dihydrophenarsazine 10-oxides **1** and 10-aryl-5,10-dihydrophenarsazine 10-oxides **2** react with hydrochloric, hydrobromic, trichloroacetic acids, and pentachlorophenol, only protonation at the oxygen atom occurs with formation of addition products in salt form ≡AsO···HX [1].

In the case of hydriodic acid, we have observed [2] rather facile cleavage of the arsenic–carbon bond. Thus upon heating in an alcohol–water medium, as the major product of reaction between As oxides **1** and HI we identified 10-iodo-5,10-dihydrophenarsazine (**3**), while in the case of As oxides **2** we identified diphenylamine (**4**) (see reactions (1) and (2)).



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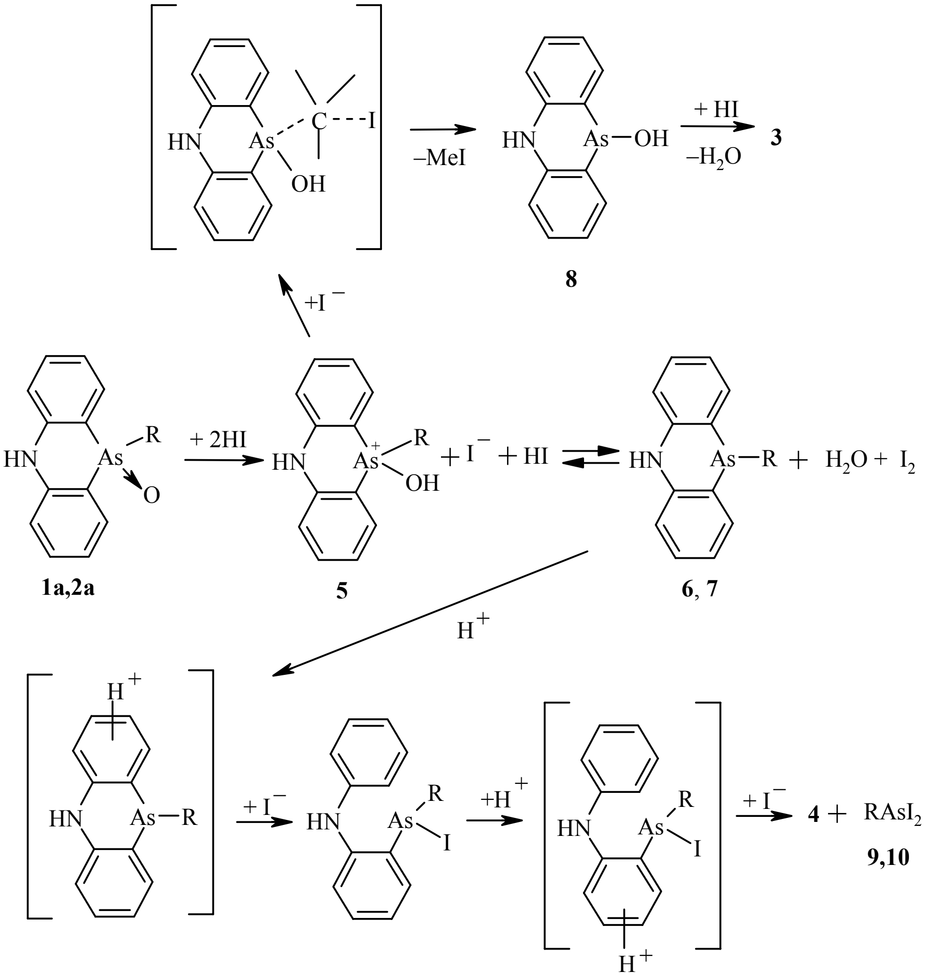
The goal of this work was to study the mechanism of the process, using as an example the reaction of 10-methyl-5,10-dihydrophenarsazine 10-oxide (**1a**) and 10-phenyl-5,10-dihydrophenarsazine 10-oxide (**2a**) with HI. The synthesis was carried out according to the procedure described in [2]. We used high-resolution mass spectrometry to study the starting compounds, the reaction mixtures, and the isolated products (Table 1).

Based on the mass spectrometric data obtained, we can hypothesize that reaction of compounds **1a** and **2a** with HI occurs according to the scheme presented below.

In the first step of the reaction, protonation of the oxygen atom on the tetracoordinated arsenic atom occurs, with formation of arsonium cations **5**, which then are reduced to form the tertiary arsines **6** and **7**. Oxidation of the latter by iodine in an alcohol–water medium has been well studied [3], and is a reversible process. In reaction of 10-methyl-5,10-dihydrophenarsazine 10-oxide (**1**), the arsonium cation **5** (R = Me) formed in the first step as a result of attack by the iodide anion according to an S_N2 mechanism can be converted to 10-hydroxy-5,10-dihydrophenarsazine (**8**), which when treated with HI gives compound **3**; reaction (1) does not occur for compound **2**.

Dihydrophenarsazine **6** or **7** formed in the first step then is protonated at the benzene ring of the 5,10-dihydrophenarsazine system, where the endocyclic arsenic–carbon bonds are broken to form diphenylamine (**4**) and methyldiiodoarsine (**9**) or diphenylamine and phenyldiiodoarsine (**10**).



1a, 5, 6, 9 R = Me, **2a, 7, 10** R = Ph

TABLE 1. Components of Filtrates for Reactions (1) and (2) (From Mass Spectrometry Data)

Reaction	Molecular ion*		
	empirical formula	m/z_{found}	m/z_{calc}
(1)	HI	127.9107	127.9123
	$C_{12}H_9AsIN$ (**3**)	368.8990	368.8996
	CH_3I	141.9270	141.9280
	I_2	253.8094	253.8090
	$C_{12}H_{11}N$ (**4**)	169.0928	169.0892
	CH_3AsI_2 (**9**)	343.7624	343.7541
	$C_{13}H_{12}AsN$ (**6**)	257.0174	257.0186
(2)	$C_{18}H_{14}AsNO$ (**2a**)	335.0263	335.0291
	HI	127.9129	127.9123
	I_2	253.8043	253.8090
	$C_{12}H_{11}N$ (**4**)	169.0804	169.0892
	$C_6H_5AsI_2$ (**10**)	405.7643	405.7697
	$C_{18}H_{14}AsN$ (**7**)	319. 0387	319.0342

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* Ion peaks containing the most abundant isotopes are indicated.

EXPERIMENTAL

The mass spectra were obtained on an MX 1310 spectrometer with ionizing electron energy of 70 eV, electron collector current of 30 μA. The substance was injected directly into the ion source by the SVP-5 direct injection system at 120°C. The exact values of the masses were determined automatically from the reference peaks of perfluorokerosene with 15000 resolution.

The Reaction of 10-Methyl-5,10-dihydrophenarsazine 10-Oxide with Hydriodic Acid was carried out according to the procedure in [2]. 50% Hydriodic acid (d = 1.56 g/cm^3) (4.5 ml, 27.4 mmol), purified by distillation over mercury to remove traces of iodine, was added to solution of 10-methyl-5,10-dihydrophenarsazine 10-oxide (**1a**) (2.01 g, 7.5 mmol) in ethanol (40 ml). The mixture was boiled for 4 h and then the solvent was distilled off to 1/5 of the initial volume. The precipitate formed upon cooling was filtered off and, after recrystallization from 1-propanol, was dried at 20-30 mm Hg above P_2O_5. Yield of compound **3** was 1.65 g (61%); mp 218-219°C (219-221°C [4]). The mass spectrum corresponded to 10-iodo-5,10-dihydrophenarsine (**3**) [5]. Mass spectrum, m/z (I_{rel}, %), composition of [$M^{+\cdot}$] ion: 369 (2.7), 242 (100.0), 214 (0.5), 167 (20.5), 166 (8.0), 151 (1.2), 139 (3.6), 125 (0.8), 113 (0.7), 77 (1.5). The filtrate was studied by mass spectrometry (Table 1).

Reaction of 10-Phenyl-5,10-dihydrophenarsazine 10-Oxide with Hydriodic Acid. Hydriodic acid (50%, 2.3 ml, 14.0 mmol) was added to solution of 10-phenyl-5,10-dihydrophenarsazine 10-oxide (**2a**) (1.00 g, 3.1 mmol) in ethanol (60 ml). The mixture was boiled for 4 h and then the solvent (3/4 of volume) was distilled off. The residue was dissolved in acetone (30 ml) and treated with a mixture of solution of potassium hydroxide (1.57 g) in water (100 ml) and benzene (100 ml) and then filtered; the benzene layer was removed and dried with anhydrous calcium chloride. The residue after distilling off the solvent, recrystallized from aqueous ethanol (1:1), has mp 53°C (compare with literature data in [6]). Yield 0.20 g (39%). The mass spectrum corresponds to diphenylamine. Mass spectrum, m/z (I_{rel}, %), composition of the ion: 170 (12.2), 169 (100.0) [$M^{+\cdot}$], 168 (47.3), 167 (28.1), 166 (6.1), 77 (11.2), 66 (9.5), 65 (7.1), 51 (13.8), 39 (7.3). The filtrate was studied by mass spectrometry (Table 1).

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