ORGANO ARSENIC COMPOUNDS

II. N,N-DIALKYL AMIDODIFLUOROARSENITES AND N-ALKYL IMIDOFLUOROARSENITES[1]

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ABSTRACT

The reaction of arsenic fluoride with aliphatic amines was studied. Secondary amines gave N,N-dialkyl amidodifluoroarsenites. Primary amines while reacting similarly lose HF subsequently and yield N-alkyl imidofluoroarsenites.

The reaction of aliphatic primary and secondary amines with arsenic trichloride was examined in the first part of this work (1). We report now the behavior of these amines towards arsenic trifluoride. On reacting gaseous ammonia and arsenic trifluoride, Besson (2) obtained a solid addition product, $2AsF_3.5NH_3$. Woolf and Greenwood (3) examined the complex formation of arsenic trifluoride. They found that arsenic trifluoride gives less stable complexes than boron trifluoride or antimony pentafluoride.

By adding 2 moles of a secondary amine to 1 mole of arsenic trichloride in benzene solution, N,N-dimethylamido-, N,N-diethylamido-, and piperidino-difluoroarsenites were synthesized according to the following equation:

$$AsF_3 + 2R_2NH \rightarrow R_2NAsF_2 + R_2NH.HF.$$

After the amine hydrofluoride was filtered off, the amidodifluoroarsenites were purified by vacuum distillation and obtained as colorless liquids. All these compounds have characteristic odors and are sensitive to hydrolysis.

TABLE I
Amidodifluoroarsenites
$R'R''NAsF_2$

R′	R″	Boiling point, °C/mm	Refractive index, n_D^{20}	Nitrogen, %		Fluorine, %		Yield, %	Molecular weight	
				Calc.	Found	Calc.	Found		Calc.	Found
Methyl	Methyl	43–44/40	1.4461	8.92	8.89	24.20	24.3	59	157	182
Ethyl	Ethyl	39–40/20	1.4857	7.57	7.59	20.53	20.8	75	185	204
Piperidyl		44–45/10	1.4920	7.10	7.09	19.28	19.5	69	197	206
Cyclohexyl	H	94/9*	—	6.63	6.75	18.00	18.3	67	211	218

*M.p. 65–66.

Some aliphatic primary amines were also reacted with arsenic trifluoride under the same conditions which were used with the secondary amines. Ethyl-, *i*-propyl-, and *t*-butyl-amines gave the corresponding N-alkyl imidofluoroarsenites.

$$\begin{aligned} AsF_3 + 2RNH_2 \rightarrow\ & RNHAsF_2 + RNH_2.HF \\ & \quad \downarrow -HF \\ & R\text{—}N\text{=}As\text{—}F \end{aligned}$$

The latter compounds can be all distilled in vacuum without decomposition. However,

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they are sensitive towards hydrolysis. Their molecular weights are 2 to 4 times greater on the basis of the freezing point depressions of benzene solutions than the calculated values for the monomeric formula shown in the above equation. Consequently they are similar to the arsenimides of other type (4) and may be characterized as low molecular weight polymers.

The reaction of arsenic trifluoride with cyclohexylamine under similar conditions did not give N-cyclohexyl imidofluoroarsenite, but instead yielded N-cyclohexyl amidodifluoroarsenite. In this case the primary amine derivative did not lose hydrogen fluoride to form the corresponding imidofluoroarsenite.

TABLE II
Imidofluoroarsenites
$(RNAsF)_n$

R	Boiling point, °C/mm Hg	Refractive index, n_D^{20}	Nitrogen, % Calc.	Nitrogen, % Found	Fluorine, % Calc.	Fluorine, % Found	Yield, %	Molecular weight Calc. (monomeric)	Molecular weight Found
Ethyl	180–182/12	1.5752	10.23	10.61	13.90	13.4	60	137	560
i-Propyl	150–155/9	1.5492	9.27	9.22	12.58	12.6	63	151	775
t-Butyl	91–92/8*	—	8.48	8.52	11.51	11.7	67	175	360

*M.p. 90–91.

EXPERIMENTAL

Arsenic trifluoride was prepared according to Russel, Rundle, and Yost (5), distilled twice, and stored in a polyethylene flask. Absolute benzene and available purest anhydrous amines were used. The work was carried out with the strictest exclusion of air and moisture. The use of arsenic trifluoride (6) and the fluoroarsenite products require careful work since these arsenic compounds have both the properties of arsenic and hydrogen fluoride regarding vapor and contact effect. For molecular weight determination, the freezing point depression of benzene solutions was used.

N,N-*Dialkyl Amidodifluoroarsenites*

A solution of 0.2 mole of the secondary amine in 50 ml toluene (or benzene) was added slowly to a mixture of 13.2 g (0.1 mole) arsenic trifluoride and 150 ml toluene (or benzene) between 0 and 10° C under cooling and effective stirring. The amine hydrofluoride started to precipitate as soon as the amine addition began. After the addition of the amine was completed, the reaction mixture was kept for an additional 15 minutes below 0° C and then was allowed to come to room temperature. The stirring was continued at room temperature for about 1 hour. Then the amine hydrofluoride was filtered by suction and washed carefully with a small amount of toluene (benzene). From the clear filtrate so obtained the solvent was removed by distillation between 50 and 100 mm. This left the raw products behind as a yellow liquid. It was purified by fractionation in vacuum. In this manner the N,N-dimethylamido-, N,N-diethylamido-, and piperidino-difluoroarsenites were obtained as colorless liquids with an unpleasant smell. Yields, physical data, and analytical data of the compounds are shown in Table I.

N-*Alkyl Amidodifluoroarsenites*

Starting from 0.2 mole of the corresponding primary amine (ethyl-, *i*-propyl-, or *t*-butyl-amine) and 13.2 g (0.1 mole) arsenic trifluoride, the preparations were carried out in the same manner as that described for N,N-dialkyl amidodifluoroarsenites. After the solvent was removed by distillation, the raw product remaining was fractionated in vacuum. The N-ethyl- and N-*i*-propyl-imidofluoroarsenites were obtained as almost colorless and odorless liquids. The N-*t*-butyl imidofluoroarsenite solidified to white crystals. Physical and analytical data and the yields of the compounds prepared are shown in Table II.

N-*Cyclohexyl Amidodifluoroarsenites*

Benzene solutions of 19.8 g (0.2 mole) cyclohexylamine and 13.2 g (0.1 mole) arsenic trifluoride were reacted in the manner used with previous examples. After being filtered by suction, the cyclohexylamine hydrofluoride was washed with benzene. The filtrate containing the main product was distilled. At first benzene was distilled over and then at 95° C/9 mm N-cyclohexyl amidodifluoroarsenite, which solidified to white crystals melting at 65–66° C. Further data are shown in Table I.

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