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Abstract

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ON SOME ORGANOARSENIC DERIVATIVES OF ETHYLENIMINE

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The interaction of organoarsenic compounds with ethylenimine has not been studied up to now. It seemed to us of interest to obtain N-substituted organoarsenic derivatives of ethylenimine. In the presence of triethylamine, by the interaction of ethylenimine with mono- and dialkyl-substituted haloarsines, we succeeded for the first time in obtaining, respectively, mono- and diethylenimides of alkyl-(aryl)- and dialkylarsinous acids according to the scheme:

$$R_2AsX + HN\begin{matrix}CH_2\\CH_2\end{matrix} + (C_2H_5)_3N \rightarrow R_2As{-}N\begin{matrix}CH_2\\CH_2\end{matrix} + (C_2H_5)_3N \cdot HX.$$

$$RAsX_2 + 2HN\begin{matrix}CH_2\\CH_2\end{matrix} + 2C_2H_5N \rightarrow RAs\left[N\begin{matrix}CH_2\\CH_2\end{matrix}\right]_2 + 2(C_2H_5)_3N \cdot HX.$$

The compounds obtained are colorless, soluble in ether, acetone, and benzene, and hydrolytically unstable. Some of their physical properties are given in Table 1.

Table 1

Mono- and diethylenimides of alkyl-(aryl)-arsinous acids

No.	R	Gross formula	Yield, %	B.p., °C (P in mm)	d_4^{20}	n_D^{20}	MR_D	AR_{As}	As, % found	As, % calculated	N, % found	N, % calculated
1	C_2H_5	$C_6H_{12}NAs$	74	55 – 54 (8)	1.2149	1.5051	49.92	11.60	39.68	39.83	–	–

No.	R	Gross formula	Yield, %	B.p., °C (P in mm)	d_4^{20}	n_D^{20}	MR_D	AR_{As}	As, % found	As, % calculated	N, % found	N, % calculated
2	*n*-C_3H_7	$C_6H_{15}N_2As$	10.0	48 – 49 (2)	1.1992	1.5080	50.24	11.33	36.80	37.06	13.60	13.86
3	C_6H_5	$C_{10}H_{13}N_2As$	76.4	100 – 101 (1)	1.6010	1.3276	60.93	11.77	31.50	31.72	11.65	11.76
4	C_2H_5	$C_5H_{14}N_2As$	24.06	47 – 48 (18)	1.1399	1.4820	43.76	–	42.80	42.78	–	–
5	*n*-C_3H_7	$C_8H_{18}N_2As$	55.4	48 (2)	1.1023	1.4927	53.55	11.86	36.82	36.87	7.04	6.89
6	*n*-C_4H_9	$C_{10}H_{22}N_2As$	77.7	74 (1)	1.0803	1.4970	62.62	11.60	32.54	32.40	5.45	6.06

Reaction with alkyl halides and water leads to cleavage of the As–N bond. For example, the monoethylenimide of di-*n*-propylarsinous acid reacted with methyl iodide, giving β-iodoethyl-N-trimethyliodoammonium (1). Benzyl bromide with the ethylenimide of dialkylarsinous acids gave resin-like products that were difficult to purify. The diethylenimide of phenylarsinous acid reacted with water, forming phenylarsine oxide and ethylenimine.

In order to obtain triethylenimide, the reaction of arsenic trichloride with ethylenimine was carried out, but it was not successful. Repeated attempts to isolate the reaction product ended in explosions during distillation.

The calculated data indicate that in the mono- and diethylenimides of alkyl-(aryl)-arsinous acids obtained, the average value of AR_{As} is equal to 11.63.

The infrared absorption spectra of the compounds obtained, which we studied, confirm the proposed structure. Thus, in the spectra of the ethylenimides of di-*n*-propyl-, di-*n*-butyl-, and diethylenimide of *n*-propylarsinous acids, low-intensity absorption bands are observed at 570 cm^{-1}, characteristic

Fig. 1. IR absorption spectra of mono- and diethylene imides of alkyl-(aryl)arsinic acids.
1 –ethylene imide of di-*n*-propylarsinic acid, 2 –diethylene imide of *n*-propylarsinic acid, 3 –ethylene imide of di-*n*-butylarsinic acid, 4 –diethylene imide of phenylarsonic acid.

Fig. 1. IR absorption spectra of mono- and diethylene imides of alkyl-(aryl)arsinic acids. 1 —ethylene imide of di-*n*-propylarsinic acid, 2 — diethylene imide of *n*-propylarsinic acid, 3 —ethylene imide of di-*n*-butylarsinic acid, 4 —diethylene imide of phenylarsonic acid

Figure 1: Fig. 1. IR absorption spectra of mono- and diethylene imides of alkyl-(aryl)arsinic acids. 1 —ethylene imide of di-*n*-propylarsinic acid, 2 —diethylene imide of *n*-propylarsinic acid, 3 —ethylene imide of di-*n*-butylarsinic acid, 4 — diethylene imide of phenylarsonic acid

for the As–C bond ([2]). In the case of the diethylene imide of phenylarsonic acid, this absorption band should, in all probability, be shifted toward higher frequencies owing to possible interaction of the *p*-electrons of the atom with the π-electrons of the benzene ring and, apparently, is superimposed on the absorption band with a maximum at 690 cm^{-1}, characteristic of a monosubstituted benzene ring. In the spectra of all the compounds obtained, intense narrow absorption bands are observed at 1230 cm^{-1} and 890 cm^{-1}, indicating the presence in the compound of a substituted ring $-N\begin{matrix}/CH_2\\ \backslash CH_2\end{matrix}$.

Noteworthy is the higher value of the corresponding frequencies in comparison with unsubstituted ethylenimine (1215 and 855 cm^{-1}) (3). Another undoubted proof of the presence of the ethylenimine ring is the presence in the IR spectra of intense absorption at 3040 cm^{-1}, which is characteristic of stretching vibrations of the C–H bond of the ring (4).* (see Fig. 1). The IR spectra were obtained on an IR-10 spectrophotometer between KBr plates.

Experimental Part

1. **Preparation of diethylenimide of ethylarsonous acid (I).** To a mixture of 50 g (0.12 mole) of ethylenimine and 13.7 g (0.135 mole) of triethylamine in 80 ml of dry ethyl ether, with strong cooling and in a stream of nitrogen, with constant stirring, 10.1 g (0.06 mole) of ethyldichloroarsine in 100 ml of ether was slowly added. After completion of the addition of the arsine, the reagent mixture was stirred for 2 h at room temperature. After separation of triethylamine hydrochloride and evaporation of the ether in vacuo, the residue in the flask was distilled. A fraction with b.p. 53–54° (8 mm) was isolated. Yield 17.4% of theory. d_4^{20} 1.2149; n_D^{20}, 1.5051; MR_D found 49.92, AR_{As} 11.60.

$C_6H_9N_2As$. Found %: As 39.68
Calculated %: As 39.83

Diethylenimides of *n*-propyl-(II) and phenyl-(III) arsonous acids were obtained analogously.

2. **Preparation of ethylenimide of di-*n*-propylarsonous acid (V).** From a mixture of 3.0 (0.07 mole) of ethylenimine, 8.0 g (0.08 mole) of triethylamine in 80 ml of ether and 16.8 g (0.08 mole) of di-*n*-propylbromoarsine in 100 ml of ether, (V) was obtained in 55.1% yield, with b.p. 48° (2 mm), d_4^{20} 1.1023, n_D^{20} 1.4927; MR_D found 53.55, AR_{As} 11.86.

$C_8H_{18}NAs$. Found %: As 36.82; N 7.04
Calculated %: As 36.87; N 6.89

3. **Reaction of (V) with methyl iodide.** 2.0 g of (V) was treated, with cooling, with an excess of freshly distilled methyl iodide. The precipitated microcrystalline yellow solid was washed with ether and dried. The substance is insoluble in water and in ordinary organic solvents. On heating to 210°, without melting, it was completely resinified. Qualitatively, arsenic is absent.

Found %: C 18.07; H 4.24; N 4.17; I 74.28
Calculated %: C 17.61; H 3.84; N 4.11; I 74.44

The product obtained—β-iodoethyl-*N*-trimethyliodoammonium—is identical with that indicated in the literature.

By reaction of mono- and dialkyl-(aryl)-haloarsines with ethylenimine, mono- and diethylenimides of alkyl-(aryl)-arsonous acids, not previously described in the literature, have been obtained for the first time, and their IR spectra have been studied.

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Note: Figure translations are in progress. See original paper for figures.