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Abstract

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Sulfur-Containing Organic Compounds of Arsenic

Preparation of β-Diethylaminoethyl S-Esters of Certain Thio Acids of Trivalent Arsenic

(Presented by Academician A. E. Arbuzov, March 9, 1964)

In continuation of our previous studies (^{1,2}) on the synthesis of thioesters of acids of trivalent arsenic and with the aim of obtaining new organoarsenic physiologically active compounds, the interaction of β-diethylaminoethyl mercaptan with arsenic chlorides was studied. According to the general reaction scheme (I) given below, from β-diethylaminoethyl mercaptan and the corresponding arsenic chlorides in dry ethyl ether in the presence of triethylamine, the hitherto unknown β-diethylaminoethyl S-esters of thioarsenious, ethylthioarsinous, phenylthioarsinous, and diphenylthioarsinous acids were synthesized.

$$\begin{gathered}(3-n)\,\mathrm{Et_2NCH_2CH_2SH} + \mathrm{R}_n\mathrm{AsCl}_{(3-n)} + (3-n)\,\mathrm{Et_3N} \rightarrow \\ \rightarrow (3-n)\,\mathrm{Et_3N}\cdot\mathrm{HCl} + \mathrm{R}_n\mathrm{As}\,(\mathrm{SCH_2CH_2NEt_2})_{(3-n)}\,, \end{gathered} \tag{I}$$

where $n = 0, 1, 2$; R is alkyl or aryl.

Some analytical data, physical constants, and yields of the synthesized thioesters are given in Table 1. The thioesters are thick oily liquids with a weak but specific odor and are slightly yellow in color. They dissolve well in acetone, benzene, and alcohol. They are insoluble in water and stable in it. On prolonged storage in air they are slowly oxidized by atmospheric oxygen, liberating the corresponding disulfides and arsenic oxides, for example:

$$4(\mathrm{Et_2NCH_2CH_2S})_3\mathrm{As} + 3\mathrm{O_2} \rightarrow 2\mathrm{As_2O_3} + 6(\mathrm{Et_2NCH_2CH_2})_2\mathrm{S_2}.$$

The complete β-diethylaminoethyl S-ester of thioarsenious acid is thermally unstable and decomposes on distillation in vacuo. It was analyzed in "crude" form.

We obtained the N-hydrochlorides of β-diethylaminoethyl S-esters of acids of trivalent arsenic by reacting β-diethylaminoethyl mercaptan with the corresponding arsenic chlorides in absolute ethyl ether according to the general scheme II.

$$(3-n)\,\mathrm{Et_2NCH_2CH_2SH{+}R_nAsCl_{3-n}} \rightarrow \left[\mathrm{R_nAs}\left(\mathrm{SCH_2CH_2\overset{+}{N}HEt_2}\right)_{3-n}\right]\mathrm{Cl}^-_{3-n}. \qquad \text{(II)}$$

The N-hydrochlorides of the β-diethylaminoethyl S-esters of thioarsenious, ethylthioarsinous, phenylthioarsinous, *p*-nitrophenylthioarsinous, and diphenylthioarsinous acids presented in Table 2 are white crystalline compounds. They dissolve very well in water, methanol, and ethanol and are insoluble in ethyl ether, benzene, and toluene. They are stable in water, but, like the thioesters themselves, slowly decompose under prolonged exposure to atmospheric oxygen, especially at temperatures above 40–50°, liberating the corresponding arsenic oxide and di-(β-diethylaminoethyl) disulfide.

Studies of the physiological properties of the N-hydrochlorides of β-diethylaminoethyl S-esters of acids of trivalent arsenic that we obtained, carried out in the toxicology laboratory of the A. E. Arbuzov Chemical Institute,* showed that these compounds possess significant fungicidal–

* For carrying out the physiological studies, the authors express their gratitude to I. D. Neklesova and co-workers.

Table 1

No.	Compound	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	*MRD* found	*ARD* for As^{3+} found	Yield, %	Gross formula	As, % found	As, % calc.	S, % found	S, % calc.
1	$As(SCH_2CH_2NEt_2)_3$	Oil	1.1026	1.5540	137.08	11.66	98.0	$C_{18}H_{42}S_3N_3As$	15.12 14.98	15.88	20.64	20.39
2	$EtAs(SCH_2CH_2NEt_2)_2$	123–126/0.005	1.1028	1.5400	104.82	10.87	68.5	$C_{14}H_{33}N_2S_2As$	20.27 20.13	20.33	17.57 17.70	17.40
3	$PhAs(SCH_2CH_2NEt_2)_2$	173/0.005	1.1537	1.5794	120.06	11.24	65.4	$C_{18}H_{33}N_2S_2As$	18.13 18.01	17.98	15.48 15.33	15.39
4	$Ph_2AsSCH_2CH_2NEt_2$	156–157/0.0035	1.2023	1.6108	104.31	12.09	60.6	$C_{18}H_{24}NSAs$	20.85 20.47	20.73	8.92 9.07	8.87

Table 2

No.	Compound	M.p., °C	Yield, %	Gross formula	As, % found	As, % calc.	S, % found	S, % calc.	N, % found	N, % calc.	Cl, % found	Cl, % calc.
1	$[As(SCH_2CH_2\overset{+}{N}HEt_2)_3]Cl_3$	188 (decomp.)	77.8	$C_{18}H_{45}Cl_3N_3S_3As$	12.52	12.49	16.35	16.56			18.80	18.30
2	$[EtAs(SCH_2CH_2\overset{+}{N}HEt_2)_2]Cl_2$	188–190	96.5	$C_{14}H_{35}Cl_2N_2S_2As$	17.15	16.97	14.59	14.52	6.21	6.34		
3	$[PhAs(SCH_2CH_2\overset{+}{N}HEt_2)_2]Cl_2$	174 (decomp.)	82.3	$C_{18}H_{35}Cl_2N_2S_2As$	14.90	15.30	13.41	13.40	5.79	5.72		
4	$[n\text{-}NO_2C_6H_4As(SCH_2CH_2\overset{+}{N}HEt_2)_2]Cl_2^-$	158 (decomp.)	91.7	$C_{18}H_{34}Cl_2N_3O_2S_2As$	14.01	14.02	11.77	11.99				
5	$[Ph_2AsSCH_2CH_2\overset{+}{N}HEt_2]Cl$	112–114	96.6	$C_{18}H_{25}ClNSAs$	18.61	18.82	8.36	8.06				
6	$\left[\begin{matrix}CH_2-S\\CH_2-S\end{matrix}\right\rangle AsSCH_2CH_2\overset{+}{N}HEt_2\Big]Cl^-$	125–127	96.26	$C_8H_{19}ClNS_3As$	22.30	22.32	28.33	28.64				

···and weak insecticidal activity and are highly toxic toward warm-blooded animals (see Table 3).

Experimental Part

β-Diethylaminoethyl mercaptan was prepared by us from β-diethylaminochloroethylene hydrochloride and thiourea (^{3}); yield 54%, b.p. 76–78° at 39 mm.

Preparation of the β-diethylaminoethyl S-ester of diphenylthioarsinous acid. To a mixture of 4.53 g of β-diethylaminoethyl mercaptan, 3.44 g of triethylamine, and 120 ml of absolute ether, with stirring and cooling with ice water, a solution of 9.0 g of diphenylchloroarsine in 30 ml of absolute ether was added dropwise. After two hours of stirring, the precipitate of triethylamine hydrochloride was filtered off and washed with dry ether. The filtrate, after removal of the solvent in vacuo, was distilled. The following fractions were obtained: I. b.p. 155–156° at $3.5 \cdot 10^{-3}$ mm, weight 0.7 g; II. b.p. 156–157.5° at $3.5 \cdot 10^{-3}$ mm, weight 7.3 g. (For analytical data and physical constants, see Table 1.) In a manner analogous to that described earlier, from β-diethylaminoethyl mercaptan and arsenic trichloride, ethyldichloroarsine, and phenyldichloroarsine, the β-diethylaminoethyl S-esters of thioarsinous, ethylthioarsinous, and phenylthioarsinous acids were obtained, respectively (see Table 1).

Table 3

Compound	Insecticidal activity, CK_{50} (in moles/liter)	Fungal culture	Spore germination of fungi, %, at compound concentration, %: 0.05	Spore germination of fungi, %, at compound concentration, %: 0.01	Spore germination of fungi, %, at compound concentration, %: 0.005	Spore germination of fungi, %, at compound concentration, %: 0.00025	Toxicity (white mice) LD_{50}, mg/kg
$[EtAs(SCH_2CH_2NHEt_2)_2]Cl_2$ —	>1	*Alternaria radicina*	0	2	92		14 (subcutaneous)
$[EtAs(SCH_2CH_2NHEt_2)_2]Cl_2$ —	>1	*Fusicladium dendriticum*	0	2	100		14 (subcutaneous)
$[EtAs(SCH_2CH_2NHEt_2)_2]Cl_2$ —	>1	*Botrytis cinerea*	0	0	34	100	14 (subcutaneous)
$[PhAs(SCH_2CH_2NHEt_2)_2]Cl_2$ —	0.82	*Alternaria radicina*	0	2	0		10 (subcutaneous)
$[PhAs(SCH_2CH_2NHEt_2)_2]Cl_2$ —	0.82	*Fusicladium dendriticum*	0	0	0		10 (subcutaneous)
$[PhAs(SCH_2CH_2NHEt_2)_2]Cl_2$ —	0.82	*Botrytis cinerea*	0	2	0		10 (subcutaneous)

Preparation of the N-hydrochloride of the β-diethylaminoethyl S-ester of ethylthioarsinous acid. To a mixture of 10.8 g of β-diethylaminoethyl mercaptan and 100 ml of absolute ether, with vigorous stirring, a solution of 7.3 g of ethyldichloroarsine in 30 ml of absolute ether was added dropwise. After heating for half an hour on a water bath, the mixture was left at room temperature until the following day. Then the white precipitate was filtered off, washed twice with dry ether, pressed well, and dried in a vacuum desiccator to constant weight. This gave 17.3 g (instead of the expected 18.1 g) of the N-hydrochloride of the β-diethylaminoethyl S-ester of ethylthioarsinous acid with m.p. 183–188°.

For purification, the resulting N-hydrochloride was dissolved in methanol and precipitated from the solution by addition of dry ether. The product with m.p. 188–190° was analyzed (see Table 2).

Other N-hydrochlorides, listed in Table 2, were obtained analogously.

Action of water on the N-hydrochloride of the β-diethylaminoethyl ester of ethylthioarsinous acid. A solution of 2.5 g of the N-hydrochloride of the β-diethylaminoethyl S-ester of ethylthioarsinous acid in 30 ml of water was boiled for 2 h. The water was then evaporated in vacuo. The crystalline precipitate was heated with 40 ml of ether; after cooling, it was filtered off and dried in a vacuum desiccator. This gave 2.1 g, or 84.0%, of a product with mp 170–171°, which was analyzed.

Found, %: As 16.31; 16.15; S 14.86

$C_{14}H_{35}N_2S_2Cl_2As$. Calculated, %: As 16.97; S 14.52

Thus, under the conditions of the experiment described above, the N-hydrochloride under investigation undergoes no substantial changes.

Action of atmospheric oxygen on the neat β-diethylaminoethyl ester of thioarsenous acid. 6.0 g of the thioester under investigation was placed in a small flask, and well-dried air was drawn through it for 3 days. The white precipitate that separated was filtered off, washed several times with dry ether, dried to constant weight in air, and analyzed.

Found, %: As 74.07; 74.64

As_2O_3. Calculated, %: As 74.20

Distillation of the filtrate gave the main quantity of a substance with bp 122.5° at 4 mm and n_D^{20} 1.4990.

Found, %: S 24.40; 24.50

$[Et_2NCH_2CH_2]_2S_2$. Calculated, %: S 24.24

According to the literature data (^{4}), the bp of di-(β-diethylaminoethyl) disulfide is 125–135° at 5 mm.

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