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In a series of communications, diarsenites of various glycols of the general type

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Abstract

Full Text

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INTERACTION OF CERTAIN ACID CHLORIDES OF ARSENIOUS ACID WITH DIOLS

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In a series of communications, diarsenites of various glycols of the general type

$$R\begin{Bmatrix} O \\ O \end{Bmatrix} As - ORO - As \begin{Bmatrix} O \\ O \end{Bmatrix} R,$$

obtained from arsenic trichloride and glycols in the presence of a base [1–3] and by esterification of arsenious anhydride with glycols [4–6], have been described. In order to obtain mixed diarsenites, we studied the reaction of acid chlorides of dialkylarsenious acids with various diols in the presence of pyridine, taken according to the equation

$$2(R'O)_2AsCl + HOROH + 2C_5H_5N \rightarrow (R'O)_2AsORAs(OR')_2 + 2C_5H_5N \cdot HCl. \quad (1)$$

The reactions were carried out with the acid chlorides of diethyl-, dipropyl-, diisopropyl-, and dicyclohexylarsenious acids; among the diols, ethy-

Table 1

Mixed esters of arsenious acid

No.	Formula	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	Formula	As, %, found	As, %, calc.
1	C_2H_5OAs	82 (25)	1.4592	1.3201	43.10	43.25	$C_6H_{13}O_3As$	36.16	36.01
2	C_3H_7OAs	93 (17)	1.4623	1.2797	47.74	47.87	$C_7H_{15}O_3As$	33.62	33.73

*

No.	Formula	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	Formula	As, % found	As, % calc.
3	$C_6H_{11}OAs$	135–137 (23)	1.4905	1.2671	59.87	59.52	$C_{10}H_{19}O_3As$	27.48	28.59
4	iso-C_3H_7OAs	133 (20)	1.4785	1.3490	50.00	49.52	$C_7H_{15}O_4As$	31.08	31.47
5	$C_6H_{11}OAs$ *	153 (6)	1.5115	1.3608	61.28	61.17	$C_{10}H_{19}O_4As$	26.45	26.95
6	C_3H_7OAs C_6H_4	133 (18)	1.5445	1.4145	54.04	54.14	$C_9H_{11}O_3As$	30.81	30.96
7	C_2H_5OAs	143 (8)	1.4912	1.4726	52.59	53.43	$C_7H_{14}O_5NAs$	28.50	28.00
8	C_3H_7OAs *	157 (8)	1.4838	1.4044	57.24	58.04	$C_8H_{16}O_5NAs$	27.04	26.65

ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, butynediol-1,4, 2-nitro-2-ethylpropylene glycol, and pyrocatechol. The reaction was carried out in diethyl ether. However, instead of the expected diarsenite (I), on distillation we obtained trialkyl arsenite and a mixed cyclic arsenite. In the case of reactions of diethylarsenous acid chloranhydride with diethylene glycol and butynediol-1,4, only triethyl arsenite was isolated, while part of the substance remained in the distillation flask in the form of a polymer.

Table 2

Diarsenites

No.	Formula	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D found	ARD_{As} found	Formula	As, % found	As, % calc.	Yield, %
1	$(CH_2O)_2AsOCH_2CH_2OAs(OCH_3)_2$	163–164 (5)	1.5290	1.7824	59.53	0.67	$C_7H_{14}O_6As_2$	43,49	43,54	58,6
2	$(CH_2O)_2AsOCH_2CH_2OCH_2CH_2OAs(OCH_3)_2$	184–186 (9)	1.5200	1.7030	63.92	0.53	$C_8H_{16}O_7As_2$	41,75	41,84	40,9
3	$(CH_2O)_2AsOCH_2CH_2CH(CH_3)CH_2OAs(OCH_3)_2$	201–204 (6)	1.5294	1.7550	65.77	0.66	$C_8H_{18}O_6As_2$	40,12	40,05	32,4

Apparently, the diarsenite formed in the course of the reaction undergoes intramolecular disproportionation according to the scheme:

$$(R'O)_2AsOROAs(OR')_2 \rightarrow (R'O)_3As + R'OAs\begin{matrix}O\\O\end{matrix}R,$$

which is due to the possibility of formation under these conditions of a thermodynamically more stable cyclic ester of arsenous acid. It is interesting to note that tetraalkyl esters of ethylene glycol diphosphorous acid, prone to disproportionation, were obtained [7] in yields of about 50%.

For comparison, certain mixed esters of arsenous acid were synthesized from the chloranhydrides of alkylarsenous acid and glycols in the presence of pyridine; the latter are marked with an asterisk in Table 1. Some chloranhydrides of arsenous acid required for these syntheses were obtained by us from arsenic trichloride and the corresponding alcohols. Propylarsenous acid dichloranhydride: b.p. 67° (17), n_D^{20} 1,5056, d_4^{20} 1,5378.

Found, %: As 36, 22
$C_3H_7OAsCl_2$. Calculated, %: As 36, 57

Diisopropylarsenous acid chloranhydride: b.p. 74-76° (12), n_D^{20} 1,4650; d_4^{20} 1,2910.

Found, %: As 32, 46
$C_6H_{14}O_2AsCl$. Calculated, %: As 32, 78

Taking into account the tendency of alkyl diarsenites toward disproportionation, the reaction of the cyclic chloranhydride of ethylene glycol arsenous acid with certain glycols was carried out in the presence of pyridine.

presence of pyridine. In this way the diarsenites were obtained in good yields; their constants are given in Table 2. As can be seen from the data in Table 2, the value of the atomic refraction of arsenic in the diarsenites is somewhat lower than in arsenites and is on average equal to 8.63.

The esters described in Tables 1 and 2 are colorless liquids, soluble in benzene and ether and readily hydrolyzed by water. The ethyl and propyl esters of 1,3-butylene glycol arsenous acid have a pleasant odor.

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