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Abstract

Full Text

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On β,β,β-Trichloroethyl Esters of Certain Acids of Trivalent Arsenic

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The present work is a continuation of our investigations in the field of the synthesis and study of the properties of various esters of acids of trivalent arsenic ([1]). Here we set ourselves the aim of studying methods for obtaining β,β,β-trichloroethyl esters of arsenous, ethylarsinous, phenylarsinous, and diphenylarsinous acids.

We have established that, for the synthesis of the above-mentioned esters, it is very convenient to use the transesterification method, which may be expressed by the following equations:

$$(RO)_3As + 3CCl_3CH_2OH \rightarrow (CCl_3CH_2O)_3As + 3ROH.$$

$$R'As(OR)_2 + 2CCl_3CH_2OH \rightarrow R'As(OCH_2CCl_3)_2 + 2ROH.$$

It is not excluded that, for obtaining the esters, other methods may also be applied—methods that we used earlier for the synthesis of esters of acids of trivalent arsenic.

Thus, for example, the β,β,β-trichloroethyl ester of phenylarsinous acid is readily obtained from phenylarsine oxide and β,β,β-trichloroethyl alcohol on heating in vacuum:

$$C_6H_5As = O + 2CCl_3CH_2OH \rightleftarrows C_6H_5As(OCH_2CCl_3)_2 + H_2O.$$

The esters isolated by us are presented in Table 1. These esters are colorless oily liquids. In their chemical properties they are close to aliphatic esters of acids of trivalent arsenic. They are hydrolyzed by water, liberating the corresponding oxide compounds of arsenic and β,β,β-trichloroethyl alcohol.

In the interaction of acetyl chloride with the β,β,β-trichloroethyl ester of arsenous acid, arsenic trichloride was obtained, and correspondingly, with the β,β,β-trichloroethyl ester of phenylarsinous acid—phenyldichloroarsine.

Our attempts to isolate, in pure form, chloranhydrides of the composition $CCl_3CH_2OAsCl_2$ and $(CCl_3CH_2O)_2AsCl$ were likewise unsuccessful. In all probability, β,β,β-trichloroethoxydichloroarsine and di-β,β,β-trichloroethoxychloroarsine are not thermally stable; upon distillation, the following transformations chiefly occur:

$$CCl_3CH_2OH + AsCl_3 \rightleftarrows CCl_3CH_2OAsCl_2 + HCl, \quad \text{(I)}$$

$$2CCl_3CH_2OAsCl_2 \rightleftarrows (CCl_3CH_2O)_2AsCl + AsCl_3, \quad \text{(II)}$$

$$2(CCl_3CH_2O)_2AsCl \rightleftarrows (CCl_3CH_2O)_3As + CCl_3CH_2OAsCl_2, \quad \text{(III)}$$

$$(CCl_3CH_2O)_2AsCl + CCl_3CH_2OAsCl_2 \rightleftarrows (CCl_3CH_2O)_3As + AsCl_3. \quad \text{(IV)}$$

Indeed, when arsenic trichloride was heated with β,β,β-trichloroethyl alcohol, we identified only tri-β,β,β-trichloroethyl arsenite. No other individual products could be isolated.

Experimental Part

β,β,β-Trichloroethyl ester of arsenous acid. Experiment 1. A mixture of 12.67 g of triethyl arsenite and 31.0 g of β,β,β-trichloroethyl alcohol was heated to boiling in an Arbuzov distillation flask; ethyl alcohol with b.p. 78–79° was evolved in an amount of 8.35 g. By distillation in vacuum, two fractions were isolated: fraction II (b.p. 128–130°/1 mm)

Table 1

No.	Compound	b.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D	AR_D As^{3+}	As, % found	As, % calc.	Cl, % found	Cl, % calc.	Yield, %
1	$As(OCH_2CCl_3)_3$	172–173/2	1.8044	1.5351	89.75	10.01	14.18; 14.28	14.39	—	—	47.8
2	$C_2H_5OAs(OCH_2CCl_3)_2$	128–130/1.5	1.6847	1.5149	74.53	9.39	17.78; 17.85	17.99	50.9	51.08	
3	$CH_2{-}O$ $CH_2{-}O$ $AsOCH_2CCl_3$	89–90/1.5	1.7545	1.5227	49.32	10.21	26.13; 26.29	26.43	—	—	70.1
4	$C_2H_5As(OCH_2CCl_3)_2$	130/2	1.6603	1.5241	73.871	10.375	18.68; 18.48	18.69	52.61	53.08	69.7

No.	Compound	b.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D	AR_D As^{3+}	As, % found	As, % calc.	Cl, % found	Cl, % calc.	Yield, %
5	$C_6H_5As(OCH_2CCl_3)_2$	169–170/2	1.5224	1.5717	89.334	10.967	16.56; 16.59	16.69	47.10; 47.26	47.40	73.51
6	$(C_6H_5)_2AsOCH_2CCl_3$	166–167/1.5	1.4710	1.6105	89.018	12.024	19.85; 19.81	19.84	28.27; 28.89	28.18	83.17

in an amount of about 3 g, n_D^{20} 1.5149, d_4^{20} 1.6847, and the III fraction (b.p. 172–173°/2 mm) in an amount of about 15 g, n_D^{20} 1.5351, d_4^{20} 1.8044. On the basis of the arsenic analysis, fraction II was pure ethyl di-β,β,β-trichloroarsenite, and III was the β,β,β-trichloroethyl ester of arsenious acid.

Experiment 2. A mixture of 45.3 g of arsenic trichloride and 37.8 g of β,β,β-trichloroethyl alcohol was heated to boiling in a flask with a reflux condenser for 8 h. Subsequently, after repeated fractionation in vacuum, a fraction with b.p. 172–173°/2 mm and n_D^{20} 1.5352 was obtained, which corresponds to tri-β,β,β-trichloroethyl arsenite.

β,β,β-Trichloroethyl ester of ethylene glycol arsenious acid. A mixture of 12.3 g of mixed allyl ester of ethylene glycol arsenious acid and 10 g of β,β,β-trichloroethyl alcohol was heated in an Arbuzov flask; allyl alcohol was evolved, b.p. 97–99°, n_D^{20} 1.4130, in an amount of 2.7 g. After vacuum distillation, a fraction with b.p. 89–90° at 1.5 mm was isolated in an amount of 8.1 g (constants and analytical data, see Table 1).

β,β,β-Trichloroethyl ester of ethylarsonous acid. Analogously to the procedure described above, by heating a mixture of 13.0 g of the ethyl ester of ethylarsonous acid and 22.0 g of β,β,β-trichloroethyl alcohol, the β,β,β-trichloroethyl ester of ethylarsonous acid was synthesized, b.p. 132°/2 mm, in an amount of 16.2 g.

β,β,β-Trichloroethyl ester of phenylarsonous acid. Experiment 1. A mixture of 10.0 g of phenylarsonic oxide and 17.8 g of β,β,β-trichloroethyl alcohol was heated in a flask with a reflux condenser for 2 h, and then in vacuum until a constant pressure of 10 mm was established. As a result of fractionation from a Favorskii flask in vacuum, the main fraction was isolated with b.p. 169–170°/2 mm in an amount of 16.9 g.

Experiment 2. By transesterification of 9.9 g of the allyl ester of phenylarsonous acid and 10.7 g of β,β,β-trichloroethyl alcohol, 3.4 g of allyl alcohol was isolated, b.p. 96–98°, n_D^{20} 1.4145, and 9.3 g of the β,β,β-trichloroethyl ester of phenylarsonous acid with b.p. 163°/1.5 mm.

The ester is hydrolyzed by water with formation of phenylarsonic oxide.

β,β,β-Trichloroethyl ester of diphenylarsonous acid was obtained analogously to the procedure described above by heating 14.5 g of the ethyl ester

of diphenylarsonous acid and 8.0 g of β,β,β-trichloroethyl alcohol. 16.5 g of substance was isolated with b.p. 167°/1.5 mm.

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