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Gilm KAMAI, B. D. CHERNOKALSKII, and L. A. VOROB' EVA

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Abstract

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CHEMISTRY

Gilm KAMAI, B. D. CHERNOKALSKII, and L. A. VOROB' EVA

INTERACTION OF TRIALKYLARSINE OXIDES WITH ALKYL HALIDES

(Presented by Academician A. E. Arbuzov on 30 I 1962)

The structure of tertiary arsine oxides is represented by formulas (I) or (II). Their molecule has a dipole with a negative charge on the oxygen atom

$$\underset{\text{(I)}}{R_3As \rightarrow O} \qquad \underset{\text{(II)}}{R_3As = O.}$$

This structure is confirmed by studies of the dipole moments ([1]) and acid-base properties ([2]) of tertiary arsine oxides. The indicated structure suggests the possibility of addition of electrophilic reagents to the unshared electron pair of the oxygen atom. Recently, works have appeared devoted to the synthesis and study of complexes of tertiary arsine oxides with compounds in which individual atoms have unfilled electron orbitals (for example, ([3,4])).

In this connection, it seemed of interest to investigate the possibility of interaction of trialkylarsine oxides with electrophilic reagents, in particular with alkyl halides. Information on such a reaction was not found in the chemical literature. It turned out that triethylarsine oxide reacts in benzene solution, on heating, with isopropyl iodide. As a result of the reaction, a crystalline product is formed with m.p. 146-147°C, readily soluble in polar solvents and insoluble in nonpolar solvents in the cold. Elemental analysis of the substance obtained corresponded to triethyl-(triethyloxyarsoxy)-arsonium iodide III.

$$(C_2H_5)_3As—\overset{\displaystyle OH}{\overset{|}{O}}—\underset{I^-}{As^+}(C_2H_5)_3$$

$$\text{(III)}$$

In a cryoscopic study of its solution in nitrobenzene, a lower value of the molecular weight was obtained (288.5). Investigation of the electrical conductivity of solutions of triethyl-(triethyloxyarsoxy)-arsonium iodide indicated a rectilinear dependence of the molar conductivity λ (Table 1) on $\sqrt{C}$ (C is the molar concentration), which testifies that the salt obtained belongs to the strong electrolytes. The considerable electrolytic dissociation of the product may be regarded as evidence of a strongly polar or even ionic bond between the arsenic and iodine atoms.

Table 1

Electrical conductivity of solutions of triethyl-(triethyloxyarsoxy)-arsonium iodide in nitrobenzene at 25°

No.	Solution conc., mol/l	Specific electrical conductivity, $ohm^{-1} \cdot cm^{-1}$	Molar electrical conductivity, $ohm^{-1} \cdot cm^{2}$
1	$310.8 \cdot 10^{-4}$	$5.75 \cdot 10^{-4}$	18.5
2	$155.4 \cdot 10^{-4}$	$3.51 \cdot 10^{-4}$	22.59
3	$77.7 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$	25.74
4	$38.85 \cdot 10^{-4}$	$1.10 \cdot 10^{-4}$	28.31
5	$19.42 \cdot 10^{-4}$	$0.580 \cdot 10^{-4}$	29.86
6	$9.712 \cdot 10^{-4}$	$0.308 \cdot 10^{-4}$	31.72

The hydrocarbon residue of the alkyl halide does not enter into structure III. When isobutyl iodide was used instead of isopropyl iodide, a substance was obtained with the same properties as in the first case. On melting a mixed sample, no depression of the melting point was observed. Re-

the results of analysis coincided with those obtained for triethyl-(triethyloxyarsoxy)-arsonium iodide, isolated as a result of the interaction of isopropyl iodide with triethylarsine oxide.

Triethyl-(triethyloxyarsoxy)-arsonium iodide may arise, in our opinion, according to the following scheme:

$$2\,(C_2H_5)_3As^+ + O^- \rightleftarrows \begin{matrix}(C_2H_5)_3As^+ - O^- \\ \vdots \quad \vdots \\ O^- - {}^+As(C_2H_5)_3\end{matrix} \qquad (IV)$$

$$\begin{matrix}(C_2H_5)_3As^+ - O^- \\ \vdots \quad \vdots \\ -O - As^+(C_2H_5)_3\end{matrix} + JCHR - CHR'_2 \longrightarrow$$

$$\longrightarrow \left[\begin{matrix}(C_2H_5)_3{}^+As & & O^- & & CHR - CHR'_2 \\ & & & & J \\ & O^- & & & \\ & & As^+(C_2H_5)_3 & & \end{matrix}\right]^- \quad (V) \longrightarrow \left[\begin{matrix}(C_2H_5)_3As & & O & & CHR - CHR'_2 \\ & O & & J & \\ & & & As(C_2H_5)_3 & \end{matrix}\right]^-$$

$$\longrightarrow (C_2H_5)_3As\underset{-O-}{\overset{OH}{|}}As^+(C_2H_5)_3\,J^- + CHR' = CR'_2$$

$$1)\ R = CH_3,\ R' = H; \quad 2)\ R = H,\ R' = CH_3.$$

The presence of a dipole moment in the As^+—O^- bond should promote dimerization of triethylarsine oxide in benzene solution. Dimer IV reacts with an alkyl iodide through the cyclic intermediate complex V, the formation of which in the general case requires[5] less activation energy than dissociation into ions or radicals. As a result, apparently, triethyl-(triethylalkoxyarsoxy)-arsonium iodide VI is formed, which, with elimination of an olefin, is converted into triethyl-(triethyloxyarsoxy)-arsonium iodide III.

Experimental Part

Interaction of triethylarsine oxide with isopropyl iodide. A solution of 1.144 g of triethylarsine oxide and 1.09 g of isopropyl iodide in 50 ml of dry benzene was boiled for 4 hours. The crystals that precipitated upon cooling were filtered off. After recrystallization from benzene, 0.76 g (24.5%) of triethyl-(triethyloxyarsoxy)-arsonium iodide was obtained, m.p. 146-147°. The product is readily soluble in the cold in acetone, chloroform, butanol, and methanol, and insoluble in benzene.

$C_{12}H_{31}As_2JO_2$. Found, %: C 29.67; H 6.50; As 30.67; J 26.16
Calculated, %: C 29.77; H 6.45; As 30.74; J 26.21

Interaction of triethylarsine oxide with isobutyl iodide. Triethyl-(triethyloxyarsoxy)-arsonium iodide was synthesized from 2.61 g of triethylarsine oxide and 2.75 g of isobutyl iodide in 200 ml of benzene by an analogous procedure. Yield 1.58 g (22%), m.p. 146–147°. A mixed sample with the specimen from the preceding synthesis melted in the same interval.

$C_{12}H_{31}As_2JO_2$. Found, %: C 29.71; H 6.43; As 31.16; J 26.19
Calculated, %: C 29.77; H 6.45; As 30.74; J 26.21

Kazan Chemical-Technological Institute
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Note: Figure translations are in progress. See original paper for figures.