Heteroatom Chemistry
Volume 15, Number 7, 2004

The Reaction of Triphenylarsine Oxide with Ethyl Iodo-acetate Leading to Triphenyl (carboethoxy)methylarsonium Triiodide

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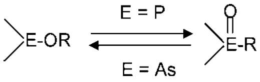
Received 22 July 2004

ABSTRACT: *New data are presented for some processes accompaning "retro-Arbuzov" reaction of tertiary arsine oxides with halogen-containing reagents. Triphenyl (carboethoxy)methylarsonium triiodide* **10a** *was obtained in the reaction of triphenylarsine oxide* **1a** *with excess of ethyl iodoacetate* **2a**. *The structure of* **10a** *was established by X-ray single crystal diffraction.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:482–485, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20050

INTRODUCTION

The Arbuzov reaction of phosphites with halogen-containing reagents is an important method of synthesis of organophosphorus compounds with the P—C and the P=O bonds [1,2]. The similar transformations in the case of organoarsenic substances failed [3–5]. Thus, it was reported that alkyl esters phenylarsinous acid or alkyl esters of diphenylarsinous acids do not appear to react with alkyl iodides at 100–120°C for 18 h [3]. The reverse reaction of tetracoordinated arsenic compounds with the As=O bond into trivalent substances (so-named "retro-Arbuzov" rearrangement) is most typical in the series of organoarsenic compounds. The differences between organophosphorus and arsenic compounds with respect of halogen-containing reagents result from the differences of thermodynamic stability of tri- and tetra-coordinated forms of the tautomeric equilibrium:



The equilibrium of tautomeric forms in the case of arsenic compounds is mostly displaced into trivalent form. In this article, new data are presented for some processes accompaning retro-Arbuzov reaction of tertiary arsine oxides with halogen-containing reagents.

RESULTS AND DISCUSSION

The reactions of tertiary arsine oxides **1** with halogen-containing reagents **2** are reported to proceed in a complicated manner [6–14]. The directions

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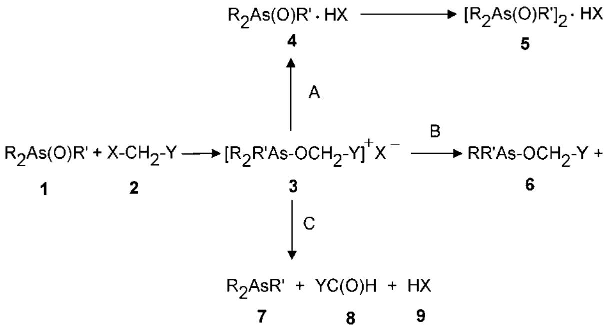
of these reactions depend upon the substituents at the arsenic atom, the nature of electrophilic reagent, and the reaction conditions. These reactions may include dehydrohalogenation (path A), retro-Arbuzov reaction (path B), and the α-elimination of alkoxy group of intermediate arsenic(III) compounds with the As-OR fragment with following reduction into tertiary arsines (path C) (reaction (1)):



(1)

The adducts **5** formed in accordance with path A were found in the solid part of the reaction mixtures when wide series of reagents were used (R = R′ = Me, Et, Pr, Hex-*c*; R = Et, Pr, Ph, R′ = C_6H_4Z, Z = OMe, NMe_2, NO_2, H, C1, Br; Y = H, Me, Et, Pr , Pr-*i*, Ph; X = Cl, Br, I) [7,8]. The formation of salts **4** was observed in a few cases. Adducts **5** may be formed by the interaction of salts **4** with the initial arsenic oxides **1** (reaction (2)) [10,11]

$$\mathbf{4} + \mathbf{1} \rightarrow \mathbf{5} \qquad (2)$$

It was also shown that the retro-Arbuzov reaction may take place in the series of tertiary trialkylarsine oxides or mixed alkyl(aryl)arsine oxides **1** (R = R′ = Et; R = Et, R′ = Ph; R = Ph, R′ = Et, Pr, Bu) by the influence of akyl halides **2** (Y = H, Me, Et, Pr; X = Br, I) [9–12]. Esters of trivalent arsenic acids **6** were isolated from the liquid part of reaction mixture with yields from 10 to 70%. In one case, the reactive alkoxyarsonium salts **3** were identified as intermediates [15]. The reactions studied were complicated by the by-formation of halo arsines that may be formed via the thermal decomposition of **4** [16]. Triphenylarsine oxide under the influence of alkyl bromides or halogen-containing reagents such as X—CH_2—Y (Y = CN, C(O)OMe, C(O)OEt, C(O)Me; X = C1, Br) transforms into **4** and **5**. In some cases, the formation of triphenylarsine was observed [14]. Thus, the retro-Arbuzov reaction does not take place in the absence of alkyl substituents at the arsenic atom.

On the basis of the data reviewed, some conclusions may be made such as

(1) The more basic trialkylarsine oxides **1** (R = R′ = A1k) predominantly behave as typical bases with the elimination of hydrogen halides from alkyl halides (path A);

(2) The less basic dialkylphenylarsine oxides and alkyldiphenylarsine oxides **1** (R = A1k, R′ = Ph; R = A1k, R′ = Ph) can react with halogen-containing reagents via the retro-Arbuzov reaction (path B). It should be noted that the retro-Arbuzov reaction contribution was increased when the basity of the initial arsine oxide was decreased (namely, with the increasing of the amount of phenyl groups on the arsenic atom).

(3) In the case of triphenylarsine oxide without readily leaving alkyl groups, the retro-Arbuzov reaction is impossible and products formed via the path A or C were found.

Path A may be considered as the result of β-elimination of **3**, confirmed by the finding of olefins in the reaction products [6,7]. Path C seems to be possible when α-elimination proceeds established by the isolation of tertiary arsines **7** and aldehydes **8** [17]. We also assumed that path C takes place when reaction conditions and nature of reagents used limit the possibility of paths A and B. These conditions seem to realize for triphenylarsine oxide that have no labile As—C_{Alk} bonds. In this case, the possibility of retro-Arbuzov reaction is limited (path B). Ethyl iodoacetate **2a** (X = I, Y = $C(O)OC_2H_5$) may be used as an electrophilic reagent. This excludes possibility of β-elimination (path A) because of absence of the protons on the β-carbon atom in **2a**. Thus, the features may be studied for the reaction proceeding via path C in its "pure" form. We have considered that tertiary arsines **7** formed via path C may lead to quaternary arsonium salts not observed earlier. This way may realized when an excess of rather reactive electrophilic reagent **2** was used. Indeed, we have found that crystalline triphenyl (carboethoxy)methylarsonium triiodide **10a** was isolated in the reaction of triphenylarsine oxide **1a** with an excess of ethyl iodoacetate **2a** at 110°C for 3 h with no solvent (reaction (3)).

$$\underset{\mathbf{1a}}{Ph_3As(O)} + \underset{\mathbf{2a}}{I\text{-}CH_2\text{-}C(O)OEt} \rightarrow \underset{\mathbf{10a}}{[Ph_3AsCH_2C(O)OEt]^+I_3^-} \qquad (3)$$

In accordance of with above-proposed scheme (reaction (1)), we have assumed that the formation of **10a** may be proceed via the following transformation series (reaction (4)):

$$\mathbf{1a} + \mathbf{2a} \rightarrow \mathbf{3a} \rightarrow \mathbf{7a} + \mathbf{8a} + \mathbf{HI} \qquad (4)$$

Under the reaction conditions, hydrogen iodide formed can react with initial **1a** to give iodine (reaction (5))

$$\underset{\mathbf{1a}}{Ph_3As(O)} + \underset{\mathbf{9}}{2HI} \rightarrow \underset{\mathbf{7a}}{Ph_3As} + H_2O + \underset{\mathbf{11}}{I_2} \qquad (5)$$

leads to **10a** (reaction (6)).

$$\mathbf{7a} + \mathbf{2a} + \mathbf{11} \rightarrow \mathbf{10a} \qquad (6)$$

Along with spectral methods (see Experimental) the molecular and crystal structure of **10a** was established by X-ray single crystal diffraction (Fig. 1). The selected bond length and bond angles are listed in Table 1. The arsenic atom has the tetrahedral configuration and triiodide anion has a linear structure.

EXPERIMENTAL

General Data

The IR spectra were obtained in KBr pellets with an UR-20 infrared spectrophotometer. The ^{1}H NMR spectra were taken on a Bruker WM 250 (250 MHz) instrument in $CDCl_3$ with $(Me_3Si)_2O$ as an internal reference.

X-ray Crystallography

Crystal cell data of **10a** were measured on an Enraf-Nonius CAD-4 four circle diffractometer fitted with graphite monochromatized Mo K_α radiation, $\lambda = 0.7103$ Å, employing the $\omega/2\Theta$ technique to $\Theta \leq 26.29°$. From 5484 reflections measured, 2847 were assumed as observed applying the conditions $I \geq 3\sigma(I)$. The final disagreement indices are $R = 0.037$, $R_w = 0.085$ for observed reflections. Crystal data for **10a** are monoclinic, space group $P2_1/n$, $a = 10.992(3)$, $b = 13.875(2)$, $c = 17.216(3)$ Å, $\beta = 100.83(8)°$, $V = 2579(1)$ Å^3, $d_{Calc} = 1.99$ g/m^3, $Z = 4$. Data were corrected for the absorption effect (μMo 4.9 cm^{-1}). The structure was solved by direct method using the SIR program [17] and refined by the full matrix least squares using SHELXL97 program [18]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated position with thermal parameters 30% larger than atom to which they attached. All calculations were performed carried out using WinGX program [19]. Cell parameters, data collection, and data reduction were performed on Alpha Station 200 computer using MoLEN program [20]. All figures were made using the program PLATON [21]. (CCDC 242983 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre 12. Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033; or deposit@ccdc.cam.ac.uk.)

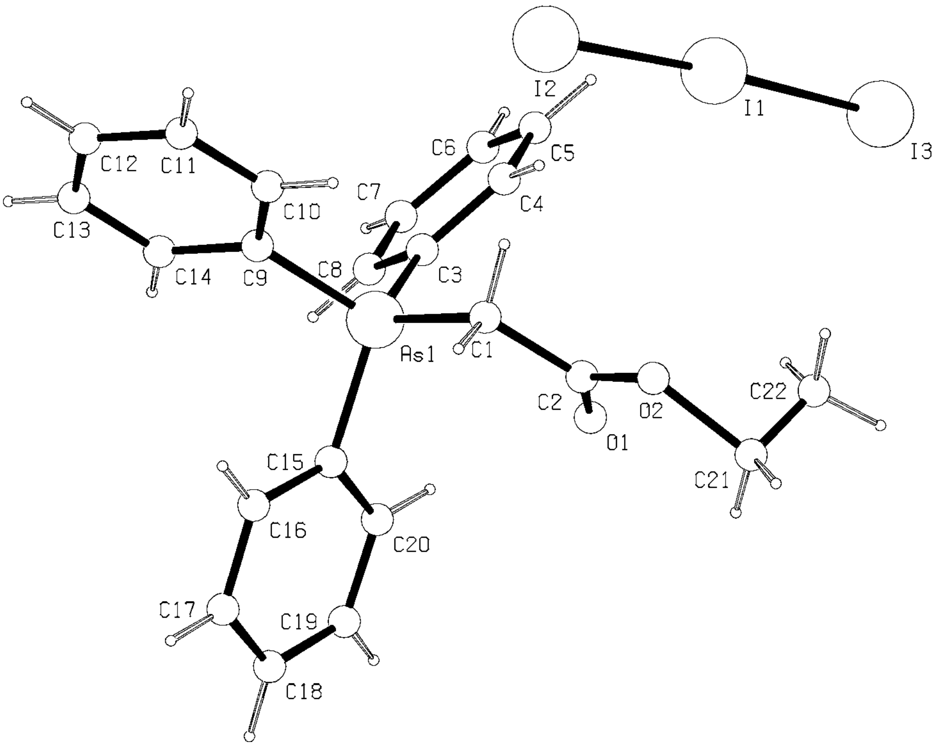


FIGURE 1 Molecular structure of the ions of **10a**.

TABLE 1 Selected Bond Lengths (Å) and Bond Angles (°) in **10a**

Bond Lengths			
I1–I2	2.918(2)	C1–C2	1.501(10)
I1–I3	2.939(2)	O2–C2	1.313(10)
As1–C1	1.921(7)	O1–C2	1.189(9)
As1–C3	1.911(7)	C21–C22	1.23(3)
As1–C9	1.906(7)	O2–C21	1.57(2)
As1–C15	1.911(7)		
Bond Angles			
I2–I1–I3	177.14(9)	C1–As1–C3	110.3(3)
As1–C15–C16	117.7(5)	C1–As1–C15	111.4(3)
As1–C15–C20	121.1(5)	C3–As1–C9	109.7(3)
As1–C1–C2	111.4(5)	C1–As1–C9	106.5(3)
As1–C3–C4	121.2(5)	C9–As1–C15	107.9(3)
As1–C3–C8	119.0(5)	C3–As1–C15	110.9(3)
As1–C9–C10	121.0(5)	O2–C21–C22	98(2)
As1–C9–C14	119.2(5)	O1–C2–O2	125.9(7)
O1–C2–C1	124.2(7)	C2–O2–C21	117.4(7)
O2–C2–C1	109.9(6)		

*Triphenyl (carboethoxy)methylarsonium triiodide (**10a**)*

The mixture of **1a** (3.6 g, 11.2 mmol) and **2a** (15.9 g, 74.3 mmol) was heated in a sealed tube at 110°C for 4 h. The mixture was evaporated at reduced pressure (40 mmHg) at 100°C for 2 h. The residue was diluted by ethanol. Product **10a** (1.8 g, 22%) was isolated from the residue by reprecipitation with diethyl ether. Compound **10a** was recrystallized with ethyl acetate, mp 120–122°C. IR (vaseline oil): $\nu_{\max}$ 3082 (C–H, Ph), 1718 ν (C=O), 1575 ν (C=C, Ph), 1460 δ_{as} (CH_3), δ (CH_2), 1450 ν (C=C, Ph), 1380 δ_s (CH_3), 1300, 1180 ν (C–O). ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3H, $\underline{CH_3}CH_2O$, $^3J_{HH}$ 7.0), 3.93 (q, 2H, $CH_3\underline{CH_2}O$, $^3J_{HH}$ 7.0), 4.38 (broad s, 2H, $\underline{CH_2}As$), 7.48 (m, 15H, $C_6\underline{H_5}$). Anal. Found: C, 34.15; H, 2.98. $C_{22}H_{22}AsI_3O_2$ requires C, 34.12; H, 2.87%.

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