REACTIONS OF TERTIARY ARSINE OXIDES WITH MERCAPTANS

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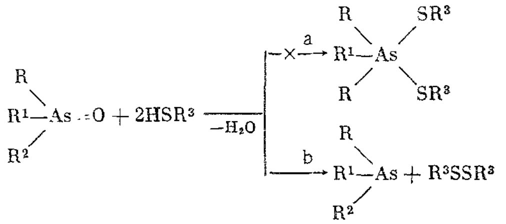
The reactions of tetracoordinated organoarsenic compounds, which contain the arsenyl grouping (As =O), with mercaptans can proceed in an ambiguous manner. Arsonic and arsinic acids [1-4], and the alkyl esters of tetracoordinated arsenic acids [5], react with mercaptans to give the esters of tricoordinated arsenic thioacids. It was reported in [6] that pentacoordinated cyclic arsenic thio compounds are formed when dialkylarsinic acids are reacted with 1,2-ethanedithiol. Information is lacking in the literature on the reactions of tertiary arsine oxides with mercaptans.

It is possible to propose two directions for the reactions of tertiary arsine oxides with mercaptans.

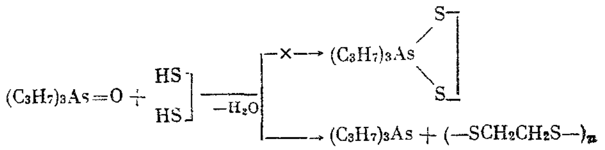


$R=R^1=R^2=C_2H_5$
$R=R^1=R^2=C_3H_7$
$R=R^1=C_2H_5$; $R^2=C_6H_5$
$R=C_2H_5$; $R^1=R^2=C_6H_5$
$R=R^1=R^2=C_6H_5$

$R^3=C_4H_9$
$R^3=C_6H_5$
$R^3=C_2H_5$
$R^3=C_3H_7$
$R^3=C_4H_9$

The formation of the pentacoordinated arsenic thioester and water can be expected in the case of direction *a*, and in the case of direction b the formation of the tertiary arsine, dialkyl(diaryl) disulfide, and water. Our studies disclosed that in all cases the reactions of tert-arsine oxides with mercaptans are oxidation–reduction reactions and go along direction b.

When tripropylarsine oxide is reacted with 1,2-ethanedithiol we obtained tripropylarsine and poly(ethyl disulfide), and not the cyclic pentacoordinated arsenic thioester.



All of the syntheses were carried out in benzene medium in a nitrogen atmosphere; the formed water was removed from the reaction mixture by azeotropic distillation. The reaction products were separated either by vacuum distillation or recrystallization. The structure of the obtained tertiary arsines and dialkyl(diaryl) disulfides was confirmed by elemental analysis. The physical constants of the compounds were close to the literature data (Table 1). In addition, the structure of diethylphenylarsine and ethyldiphenylarsine was confirmed by the IR spectra.

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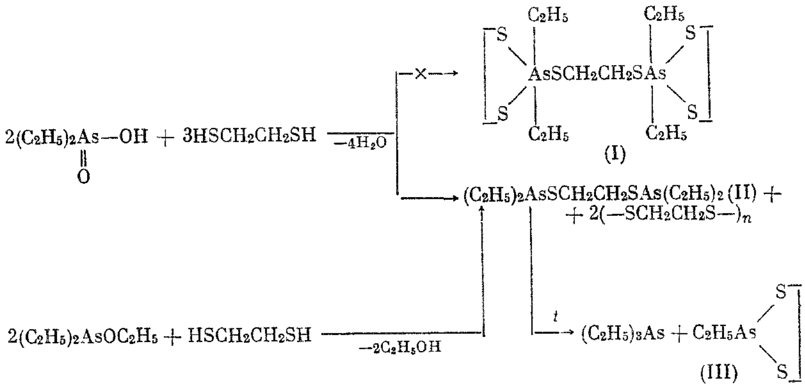
TABLE 1

Starting compounds	Reaction products	Yield, %	bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Empirical formula	Element	$\frac{\text{Found}}{\text{Calculated}}$, %
$Et_3As{=}O + 2BuSH$	Et_3As [7]	20,4	47—48 (28)	1,4735	1,0725	$C_6H_{15}As$	As	$\frac{45{,}94}{46{,}21}$
	BuSSBu [5]	92,8	98—98,5 (9)	1,4930	0,9567	$C_8H_{18}S_2$	S	$\frac{35{,}62}{35{,}89}$
$Pr_3As{=}O + 2PhSH$	Pr_3As [7]	76,5	73—75 (9)	1,4725	1,0213	$C_9H_{21}As$	As	$\frac{36{,}45}{36{,}76}$
	PhSSPh [8]	77,0	mp 60—62 (methanol)	—	—	$C_{12}H_{10}S_2$	S	$\frac{29{,}55}{29{,}37}$
$Et_2As(O)Ph + 2EtSH$	Et_2AsPh [9]	71,0	96—98 (8)	1,5592	1,1721	$C_{10}H_{15}As$	As	$\frac{35{,}64}{35{,}24}$
	EtSSEt [8]	54,1	35(9)	1,5040	0,9926	$C_4H_{10}S_2$	S	$\frac{52{,}52}{52{,}45}$
$EtAs(O)Ph_2 + 2PrSH$	$EtAsPh_2$ [10]	73,4	98,5—100(0,02)	1,6183	1,2377	$C_{14}H_{15}As$	As	$\frac{28{,}88}{29{,}00}$
	PrSSPr [11]	74,6	67 (9)	1,4986	0,9597	$C_6H_{14}S_2$	S	$\frac{42{,}54}{42{,}66}$
$Ph_3As{=}O + 2BuSH$	Ph_3As [7]	65,7	mp 58—59 (ethanol)	—	—	$C_{18}H_{15}As$	As	$\frac{24{,}43}{24{,}51}$
	BuSSBu	58,6	97—99,5 (9)	1,4946	—	$C_8H_{18}S_2$	S	$\frac{35{,}78}{35{,}89}$
$Pr_3As{=}O + (HS{-}CH_2)_2$	Pr_3As	50,2	75—77 (10)	1,4712	1,0214	$C_9H_{21}As$	As	$\frac{36{,}37}{36{,}76}$
	$(-SCH_2CH_2S-)_n$	85,8		—	—	$C_2H_4S_2$	S	$\frac{68{,}23}{69{,}56}$

The results reported in [6] evoked doubt on our part. When diethylarsinic acid was reacted with 1,2-ethanedithiol under the conditions given in [6] we isolated, instead of 1',2'-dithio(bis-2,2-diethyl-1,3,2-dithiaarsolanyl)ethane (I), triethylarsine, 2-ethyl-1,3,2-dithiaarsolane (III), and a white polymeric product that proved to be poly(ethylene disulfide). Apparently, in this case 1,2-dithiobis(diethylarsine)ethane (II) is formed first, which under the experimental conditions disproportionates to triethylarsine and (III). It was proved that (II) can disproportionate by reacting ethyl diethylarsinite with 1,2-ethanedithiol.



The structure of (III) was confirmed by elemental analysis, and by the IR and NMR spectra. The IR spectrum of (III) has a number of bands that can be attributed to the dithiaarsolane ring [9, 12]. Thus, the spectrum has the following skeletal vibrations in the regions (cm^{-1}): 450 m (δ_{ring}), 648 m ($\nu_{s\,C-S\text{ of ring}}$), 665 m ($\nu_{as\,C-S\text{ of ring}}$), 837 v. s (HCS +HCC +SCC +CS), 937 s (HCC +HCS), 994 w (ν_{ring}, predominantly ν_{C-C}), and also bands that belong to the stretching and deformation vibrations of the ring CH_2 groups (cm^{-1}): 2957 (ν_{asCH_2}), 2920 (ν_{sCH_2}) 1417 (δ_{CH_2}), 1285 (ω_{CH_2}), 1235 (τ_{CH_2}), 837 (ρ_{CH_2}). In addition, characteristic bands are present (cm^{-1}) at 547 ($\nu_{As-C_2H_5}$), 1460 ($\delta_{a\,sCH_3}$), 1380 (δ_{sCH_3}), 2965 ($\nu_{a\,sCH_3}$), and 2868 (ν_{sCH_3}).

The NMR spectrum of (III) has three principal groups of lines that correspond to three different groups of protons: the CH_3 group = a triplet at 1.17 ppm, the CH_2 of the ethyl radical = a quartet at 1.68 ppm, and the ring CH_2 groups = singlet at 3.01 ppm (in CCl_4 relative to TMS, 60 MHz). It was obvious that in [6] a mixture of products was present instead of (I).

From the above said it can be seen that not only arsonic and arsinic acids and their esters but also tertiary arsine oxides are reduced by mercaptans to the corresponding tricoordinated arsenic compounds. The reduction of tertiary arsine oxides by mercaptans, the same as in [13-16], can be used to obtain certain tertiary arsines.

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-10 spectrometer.

Reaction of Diethylphenylarsine Oxide with Ethyl Mercaptan. With stirring, to 21.2 g of diethylphenylarsine in a dry nitrogen atmosphere was added 11.8 g of ethyl mercaptan in 60 ml of benzene; the formed water was removed by azeotropic distillation using a Dean–Stark trap. After distilling off the solvent we isolated 6.2 g of diethyl disulfide and 14 g of diethylphenylarsine by vacuum distillation.

The other reactions were run in a similar manner (see Table 1).

The IR spectra of diethylphenylarsine and ethyldiphenylarsine have the characteristic absorption bands for the CH_2 and CH_3 groups, and those of the benzene ring (cm^{-1}): 2960 ($\nu_{a\,sCH_3}$), 2925 ($\alpha_{a\check{s}\,CH_2}$), 2870-2868 ($\nu_{sCH_3}$), 1497-1480 ($\delta_{CH_2}$), 1460-1455 ($\delta_{a\,sCH_3}$), 1385-1380 ($\delta_{sCH_3}$), 3068 and 3052 ($\nu_{=CH}$), 1595-1587 ($\nu_{C=C}$), 740 and 687 ($\delta_{CH}$), 470 [$\delta_{ring}$ of $(C_2H_5)_2ASC_6H_5$], and 478 and 465 [δ_{ring} of $C_2H_5As(C_6H_5)_2$] of a monosubstituted aromatic system. In addition, bands are present at 567 and 503 ($\nu_{As-C_2H_5}$) for $(C_2H_5)_2AsC_6H_5$ and 560 for $C_2H_5As(C_6H_5)_2$.

Reaction of Diethylarsinic Acid with 1,2-Ethanedithiol. A stirred mixture of 10.5 g of diethylarsinic acid and 8.9 g of 1,2-ethanethiol in 80 ml of benzene, contained in a flask equipped with a Dean–Stark trap, was refluxed until the water evolution ceased (3 h). After distilling off the solvent the residue was vacuum distilled. We obtained 1.1 g (21.6%) of triethylarsine with bp 33° (13 mm); n_D^{20} 1.4757; d_4^{20} 1.0765 [Found: As 45.96%. $C_6H_{15}As$. Calculated: As 46.21%], and 2.8 g (45.4%) of 2-ethyl-1,3,2-dithiaarsolane with bp

124° (14 mm); n_D^{20} 1.6594; d_4^{20} 1.5430. [Found: As 37.93; S 32.37%. $C_4H_9AsN_2$. Calculated: As 38.19; S 32.69%]. After washing with benzene, the residue from the distillation weighed 4.6 g (52.9%) and was poly(ethylene disulfide). Found: S 68.12%. $C_2H_4S_2$. Calculated: S 69.56%.

Reaction of Ethyl Diethylarsinite with 1,2-Ethanedithiol. With stirring and cooling in ice water, 3.2 g of 1,2-ethanedithiol was added to 12 g of ethyl diethylarsinite. After removal of the liberated ethanol the residue was vacuum distilled. Two products were isolated here: 1) 2.4 g (43.9%) of triethylarsine with bp 46-47° (27 mm); n_D^{20} 1.4771; d_4^{20} 1.0780. Found: As 45.92%. $C_6H_{15}As$. Calculated: As 46.21%; 2) 4.7 g (71.2%) of 2-ethyl-1,3,2-dithiaarsolane with bp 119° (10 mm); n_D^{20} 1.6627; d_4^{20} 1.5465. Found: As 38.08; S 32.52%. $C_4H_9AsS_2$. Calculated: As 38.19; S 32.69%.

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CONCLUSIONS

The reaction of tertiary arsine oxides with mercaptans is an oxidation–reduction reaction and leads to the formation of the corresponding tertiary arsines and dialkyl(diaryl) disulfides.

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