The Preparation and Properties of Compounds Containing Silicon-Oxygen-Arsenic Linkages¹

By Bertrand L. Chamberland and Alan G. MacDiarmid²

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The compounds $[(C_6H_5)_3SiO]_2AsO, [(C_6H_5)_3SiO]_2AsC_6H_5, C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5 and a polymeric material of approximate composition <math>[(C_6H_5SiO_{1.5})_{1.5})_{1.5}(AsO_{1.5})H]_x$ have been prepared and their thermal and hydrolytic properties studied.

In a previous paper³ the preparation and properties of several compounds containing Si–O–As-(III) or Si–O–As(V) linkages were reported. The preparation and hydrolytic and thermal stability of other new compounds of this type are presented in this communication.

Results and Discussion

Tris-(triphenylsilyl)-arsenate was prepared by the metathetical reaction of silver ortho-arsenate with triphenylchlorosilane according to the equation

$$3(C_{6}H_{5})_{2}SiCl + Ag_{2}AsO_{4} \xrightarrow{} 3AgCl + [(C_{6}H_{5})_{2}SiO]_{2}AsO \quad (1)$$

This product was identical with that obtained previously³ by a different reaction. A reaction analogous to that given by equation 1 using $(CH_8)_3$ -SiCl instead of $(C_6H_5)_3$ SiCl was attempted by Schmidt and Schmidbaur.⁴

Bis-(triphenylsiloxy)-phenylarsine, a crystalline compound melting at 119-120°, was isolated from the reaction of sodium triphenylsilanolate with diiodophenylarsine

$$2(C_6H_5)_2SiONa + C_6H_5AsI_2 \longrightarrow$$

 $2\text{NaI} + C_6H_5\text{As}[OSi(C_6H_5)_3]_2 \quad (2)$

A cyclic, dimeric species of composition C_6H_5As -[OSi(C_6H_5)₂O]₂AsC₆H₅, was prepared by the condensation of diphenylsilanediol with diiodophenylarsine in the presence of ammonia

 $4\mathrm{NH}_{\mathtt{s}} + 2(\mathrm{C}_{\mathtt{e}}\mathrm{H}_{\mathtt{s}})_{2}\mathrm{Si}(\mathrm{OH})_{2} + 2\mathrm{C}_{\mathtt{e}}\mathrm{H}_{\mathtt{s}}\mathrm{AsI}_{\mathtt{2}} \longrightarrow \\ 4\mathrm{NH}_{\mathtt{s}}\mathrm{I} + \mathrm{C}_{\mathtt{e}}\mathrm{H}_{\mathtt{s}}\mathrm{As}[\mathrm{OSi}(\mathrm{C}_{\mathtt{e}}\mathrm{H}_{\mathtt{b}})_{\mathtt{2}}\mathrm{O}]_{\mathtt{2}}\mathrm{AsC}_{\mathtt{e}}\mathrm{H}_{\mathtt{s}} \quad (3)$

The crystalline cyclic product melts, possibly with some change in constitution, at 145° and has the structure

$$C_6H_5As$$

O-Si(C_6H_5)2-O
AsC $_6H_5$

It may be considered a dimer of the series $[-OSi-(C_6H_6)_2OAsC_6H_6]_x$.

A resinous polymeric species of this type (x > 2) also was formed in the reaction given by equation 3. It has an identical empirical composition and infrared spectrum to that of the dimer, but it could not be isolated in the pure state and possibly contained large amounts of the dimer which could not be removed completely from the mixture.

(4) M. Schmidt and H. Schmidbaur, Angew. Chem., 71, 553 (1959).

On distilling $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$ at 350° *in vacuo*, a glassy material of identical composition but higher molecular weight was obtained. The infrared spectrum of the material indicated that the absorption maximum assigned to the Si-O-As(III) group had been displaced slightly. This substance is believed to consist chiefly of the trimer, $[-OSi(C_6H_5)_2OAsC_6H_5]_3$, mixed with some of the dimer.

A polymeric material was obtained by the cohydrolysis of arsenic trichloride with phenyltrichlorosilane. The proposed reaction is

$$C_{6}H_{5}SiCl_{3} + A_{5}Cl_{3} + 3H_{2}O \xrightarrow{NH_{4}OH} 6HCl + [C_{6}H_{5}SiO_{3}A_{5}]_{z} \quad (4)$$

The structure of the product, based on elemental analysis and infrared data, may be represented as shown below (where R is C_6H_6).



This material is analogous to a polymer containing Si-O-Al linkages reported by Andrianov, *et al.*,⁵ which had the approximate composition $[(C_6H_5SiO_{1.5})_5 \cdot AlO_{1.5} \cdot H_2O]_x$.

The product obtained in the reaction expressed in equation 4 has the approximate composition $[(C_6H_5SiO_{1.5})_8\cdot AsO_{1.5}\cdot H]_x$. Although this material is soluble in a variety of organic solvents, it does not soften or melt on heating and it appears that cross-linking must occur to a considerable extent.

The rate of hydrolysis of the solid compounds by pure water at room temperature decreases in the order $(HO)_2As(O)[OSi(C_6H_5)_2OAs(O)(OH)]_2OH >$ $[(C_6H_5)_3SiO]_3AsO > [(C_6H_5)_3SiO]_3As > C_6H_5As[OSi (C_6H_5)_2O]_2AsC_6H_5 > As[OSi(C_6H_5)_2O]_3As$, the last compound, in particular, being remarkably stable.

Whereas $[(C_6H_5)_3SiO]_3As$ distills unchanged at 350° ,³ $[(C_6H_5)_3SiO]_2AsO$, As $[OSi(C_6H_5)_2O]_2As$ and $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_6$ distill with some change in composition or constitution under similar experimental conditions.

Experimental

Reagents.—These various chemicals were identical with those used previously³: arsenic trichloride, phenyltrichloro-

⁽¹⁾ This report is based on portions of a thesis submitted by Bertrand L. Chamberland to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

⁽²⁾ Alfred P. Sloan Research Fellow.

⁽³⁾ B. L. Chamberland and A. G. MacDiarmid, THIS JOURNAL, 82, 4542 (1960).

⁽⁵⁾ K. A. Andrianov, A. A. Zhdanov and E. Z. Asnovich, Invest. Akad. Nauk S.S.S.R., Otdel. Chim. Nauk, 1760 (1959),

silane, triphenylchlorosilane, triphenylsilanol and diphenylsilanediol. Purified silver ortho-arsenate (City Chem. Corp.) and diiodophenylarsine (Eastman Organic Chemicals) were used without further purification.

Tris-(triphenylsilyl)-arsenate.—Pre-dried silver orthoarsenate (4.63 g., 10.0 mmoles), was added to triphenylchlorosilane (8.84 g., 30.0 mmoles) in 100 ml. of benzene. After stirring for 6 days at room temperature, the mixture was filtered. Evaporation of the filtrate yielded triphenylsilanol and some crude product.

The insoluble material obtained on filtration of the reaction mixture was treated with benzene in a Soxhlet apparatus for 12 hr. The benzene extract, combined with the crude product obtained from the filtrate above, was evaporated to dryness *in vacuo* and washed several times with ether to yield pure $[(C_6H_5)_3SiO]_3AsO$ (2.38 g., 26% yield, equation 1, m.p. 237-240°).

Anal.⁶ Calcd. for $C_{54}H_{45}Si_3AsO_4$: C, 70.71; H, 4.95; Si, 9.19; As, 8.17. Found: C, 70.77; H, 4.98; Si, 9.40; As, 7.95.

The infrared spectrum of the product was identical with that of the product isolated in a different reaction and reported³ previously.

Bis-(triphenylsiloxy)-phenylarsine.—Sodium triphenylsilanolate was prepared by the reaction of an excess of sodium metal with triphenylsilanol, (5.53 g., 20.0 mmoles) for 7 hr. in 200 ml. of refluxing benzene. The excess metal was then removed and diiodophenylarsine (4.08 g., 10.0 nmoles) in 20 nll. of benzene was added to the solution. A white precipitate formed immediately and the reaction mixture was refluxed for 20 minutes and filtered. An iodide analysis (as AgI) on this residue corresponded to a 95% yield of NaI (equation 2).

On evaporation, the filtrate yielded a solid which, after fractional recrystallization from ether, consisted of pure $[(C_6H_5)_3SiO]_2AsC_6H_5$ (5.4 g., 78% yield, equation 2, m.p. 119–120°).

Anal. Calcd. for $C_{42}H_{35}Si_2AsO_2$: C, 71.78; H, 5.02; Si, 8.00; As, 10.66. Found: C, 71.27; H, 4.99; Si, 8.35; As, 10.56.

The compound is soluble in benzene, ether, acetone and methanol and insoluble in petroleum ether. Its infrared absorption mexima are given in Table II.

 $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$.—Anhydrous ammonia was passed for 30 minutes through a stirred solution of diphenylsilanediol (4.32 g., 20.0 mmoles) and diiodophenylarsine (8.12 g., 20.0 mmoles), dissolved in 300 ml. of ether. The mixture was then refluxed for an additional 10 minutes and the white solid which had formed was removed by filtration and was found to contain 98% of the NH₄I expected from equation 3.

The clear filtrate was evaporated to dryness *in vacuo* at room temperature and the foam-like solid which first formed finally changed to a colorless, transparent resin on complete removal of the solvent. This product was treated with approximately 50 ml. of ether and a crystalline solid was formed in place of the resin. This solid was removed by filtration and more of the crystalline material was formed on partial evaporation of the filtrate. Several crops of crystalline material were obtained by the stepwise evaporation of the filtrate until a final volume of 5 ml. was reached, at which stage no further crystallization occurred. Complete evaporation of the ether filtrate yielded a foam-like solid which once again formed a resin upon complete removal of the solvent. This material did not crystallize on standing in a vacuum desiccator for several weeks.

All the crystalline material was combined and after washing with small quantities of ether, followed by drying *in vacuo*, pure crystalline $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$ was obtained (3.66 g., 58.6% yield, equation 3, m.p. 145°).

Anal. Calcd. for $C_{36}H_{30}Si_2As_2O_4$: C, 59.00; H, 4.13; Si, 7.67; As, 20.45. Found: C, 58.73; H, 4.25; Si, 7.52; As, 20.64; Calcd. mol. wt.: 732. Molecular weight determination⁷ by the boiling point elevation of benzene: 741.

The crystalline solid was very soluble in benzene and acetone, moderately soluble in ether and insoluble in methanol.

(6) All analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(7) Molecular weight determination performed by Geller Laboratories, Bardonia, New York. (On evaporation of benzene or acetone solutions a small quantity of resinous material—possibly a higher polymer is formed.) Its infrared absorption maxima are given in Table II.

The final resin obtained above melted in the region 43– 52° and flowed freely at 115°, was very soluble in ether, benzene and acetone and insoluble in methanol. Its infrared spectrum was identical with that of the cyclic dimeric material mentioned above.

Anal. Calcd. for $C_{36}H_{30}Si_2AS_2O_4$: C, 59.00; H, 4.13; Si, 7.67; As, 20.45; mol. wt., 732. Found: C, 58.90; H, 4.10; Si, 7.44; As, 20.90; molecular weight determination⁷ by the boiling point elevation of benzene, 687.

These results suggest that the resin consists of a mixture of species of composition $[OSi(C_6H_6)_2OAs(C_6H_5)]_x$ with the dimer predominating. A relatively small amount of higher molecular weight species might be expected to retard crystallization of the dimer from the viscous ether solutions obtained.

[($C_6H_6SiO_{1.6}$)s·(AsO_{1.6})H]_x.—A solution of 39 ml. of NIH₄OH (15 *M*) and 6 ml. of water was added slowly to AsCl₃, (18.1 g., 0.10 mole) and phenyltrichlorosilane (21.2 g., 0.10 mole), in 225 ml. of benzene over a period of 2 hr., and the mixture then was shaken vigorously for 20 minutes. The benzene phase was decanted from the white insoluble precipitate which had formed. The filtered decantate on evaporation *in vacuo* formed at first a viscous liquid which left a clear film on the glass surface, and then a foaming solid upon complete removal of the solvent. Analysis of this solid indicated a material of approximate composition [($C_6H_6SiO_{1.6}$)s·(AsO_{1.6})H].

Anal. Calcd. for $C_{48}H_{41}Si_8AsO_{14}$: C, 50.52; H, 3.62; As, 6.56; Si, 19.63. Found: C, 51.93; H, 4.23; As, 6.81; Si, 21.79.

The product did not melt but decomposed slightly at 410° (exposed to air in a melting point tube). It was very soluble in acetone; moderately soluble in benzene and nitrobenzene; slightly soluble in carbon tetrachloride and ether; and insoluble in methanol. Its infrared absorption maxima are given in Table II. The strong Si–O–As(III) peak at 893 cm.⁻¹ indicates that the material is not a mixture of $(C_6H_5SiO_{1.6})_z$ and As_2O_3 . Hydrolytic Stability.—A comparative study of the hy-

Hydrolytic Stability.—A comparative study of the hydrolytic stability of monomeric and polymeric species obtained in this and in previous work³ was carried out. Samples (0.15-0.23 g.) dissolved in either benzene or ether were placed in Petri dishes and the solvent evaporated. The films thus obtained were covered with 100 ml. of distilled water and were then allowed to stand at room temperature. After several hours the water was removed and the films were dried in an oven at 110° for 30 minutes and weighed. The weight decrease of the film was taken as a measure of hydrolysis, assuming the final hydrolysis products to be the appropriate silanol (insoluble in water) and the corresponding arsenic acid (soluble in the quantity of water employed). The results of these experiments are given in Table I. The values obtained will depend on factors such as the degree of crystallinity of the film and on its ease of being wet, or dissolved by water, in addition to the rate of chemical attack of the Si-O-As linkages.

Table I

PER CENT. HYDROLYSIS OF Si-O-As DERIVATIVES -Time under water at roomtemperature, hours 40 55 75 220 1 300 Compound C_6H_5 0 n Н -OH 0\$i—0-HOAs -Às-Ó Ċ₀H₅ Ò Ĥ Ĥ. 36 **8**6 86 - 87 2 9 1733 $[(C_6H_5)_3\mathrm{SiO}]_3\mathrm{AsO}$ 0 12 [(C₆H₅)₃SiO]₃As 1016 0 $\overline{7}$ 8 15 $[-OSi(C_6H_5)_2OAs(C_6H_5)-]_2$ 0 1 3 4 7 11 0.7 $As[OSi(C_6H_5)_2O]_3As$ 0 0 0 0.3 0.7

Thermal Stability.—The thermal stability of the compounds given below was determined by heating a sample at 350° for 30 minutes *in vacuo* with constant pumping. TABLE II

	INFRARE	d Spectra of Nev	v Si–O–As(III) De	RIVATIVES	
[(C6H5)3SiO]2AsC6H5 Wave no. (cm. ⁻¹)	[(C6H5SiO1.5)3. (AsO1.5)H] Wave no. (cm1)	[-OSi(C6H5)2OAs- (C6H5)-]2 Wave no. (cm. ⁻¹)	[-OSi(C6H6)2OAs- (C6H5)-]3 Wave no. (cm. ⁻¹)	Interpretation	Lit. Page no. ^ø or ref.
3400(m)	3420(m)	3410(m)	3420(m)	O–H stretch	
3004(w)	3060(m)	3060(m)	3020(m)	C—H stretch	56
2320(vw)					
1960(vw)	1962(w)	1960(w)	1960(w)		
1900(vw)	1893(w)	1890(w)	1888(w)		
1818(vw)	1821(w)	1820(w)	1820(w)		
1588(w)	1595(m)	1590(m)	1590(m)	C=C ring stretch	281
1485(w)	1491-1481(m)	1482(m)	1482(m)	C=C ring stretch	281
1429(m)	1434(s)	1430(s)	1430(s)	$Si-C_{6}H_{5}$ (in solid)	277-281
		1331(vw)	1331(vw)		
1299(vw)		1304(w)	1304(w)		
1259(vw)		1264(vw)	1260(w)		
1180(vw)		1181(w)	1182(w)	Si–C ₆ H₅	281
		1124(vs)	1124(vs)	Si–(C ₆ H ₆) ₂ doublet	ь
		1114(vs)	1114(vs)	Si-(C ₆ H ₅) ₂ doublet	Ъ
1114(1105)(s)	1130(vs)	、 ,			281
1081(w)		1082(m)	1076(m)		
1024(vw)		1024(vw)	1032(vw)		281
		1000(m)	1010(w)		
997(w)	995(m)	• •		Si-C ₆ H ₆	281
		962(vs)			
		• •	935(m)	Si–O–As(III) trimer	
952(m)					
877(vs)	893(s)	894(vs)		Si-O-As(III)	Ref. 3
744-737(m)	733(s)	739(s)	738(s)	Bending vib. C-H	277
710(vs)		717(vs)	716(vs)	Out of plane C–H	65
696(vs)	694(s)	697(vs)	694(vs)	Out of plane C-H	65

^a L. J. Bellamy "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954. ^b C. W. Young, P. C. Servals, C. C. Currie and M. J. Hunter, THIS JOURNAL, **70**, 3758 (1948).

 $[(C_6H_5)_3SiO]_3AsO.$ —This compound decomposed forming two crystalline bands. The most volatile band (furtherest from the heated zone) melted sharply at 142–144° (melting point of pure triphenylsilanol, 150°) and had an infrared spectrum identical with that of pure triphenylsilanol. The second, less volatile, band melted at 227° (m.p. of pure $[(C_6H_5)_3SiO]_3AsO, 242°)$ and had an infrared spectrum almost identical with that of the original material except that the Si–O–As(V) peak was much broader.

As $[OSi(C_6H_5)_2O]_3As$.—More than 96% of the sample used distilled to the cooler end of the tube and crystallized on standing. This material melted at 157° (m.p. of pure As- $[OSi(C_6H_5)_2O]_3As$, 194°) and had an infrared spectrum different from that of the starting material. The Si-O-As-(III) peak in the spectrum of As $[OSi(C_6H_5)_2O]_3As$ had split into two smaller peaks in the same region.

 $C_6H_5As[OSi(C_6H_5)_2O]_2ASC_6H_5.--Approximately 90\% of the sample used distilled and solidified as a clear dense resin in the cooler end of the tube. This product did not recrystallize on standing. The Si-O-As(III) peak at 894 cm.^{-1} in pure <math display="inline">C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$ was replaced

by a new peak at 935 cm.⁻¹ which was assumed to be the Si-O-As(III) peak in the new species formed. The infrared absorption maxima are listed in Table II.

Anal. Calcd. for $C_{54}H_{45}Si_3As_3O_6$: C, 59.00; H, 4.13; Si, 7.67; As, 20.45; mol. wt., 1098. Found: C, 59.00; H, 4.41; Si, 7.35; As, 20.28; mol. wt. determination⁷ by the boiling point in benzene, 941.

Infrared Spectra.⁸—A Perkin-Elmer, model 21, double beam recording spectrophotometer with a sodium chloride prism was used. All compounds were examined in KBr discs at concentrations of approximately 2 to 3 mg. of compound per 300 mg. of KBr. The absorption maxima of the new compounds prepared are listed in Table II.

(8) Infrared spectra of compounds mentioned in this article have been deposited as Document number 6381 with the AD1 Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.