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

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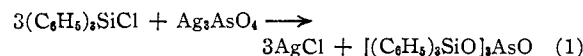
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The compounds $[(C_6H_5)_3SiO]_3AsO$, $[(C_6H_5)_3SiO]_2AsC_6H_5$, $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$ and a polymeric material of approximate composition $[(C_6H_5SiO_{1.5})_3(AsO_{1.5}H)]_x$ have been prepared and their thermal and hydrolytic properties 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.

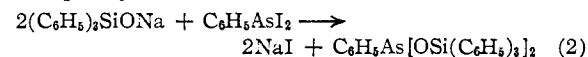
Results and Discussion

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

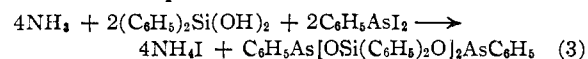


This product was identical with that obtained previously³ by a different reaction. A reaction analogous to that given by equation 1 using $(CH_3)_3SiCl$ instead of $(C_6H_5)_3SiCl$ was attempted by Schmidt and Schmidbaur.⁴

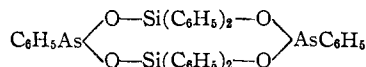
Bis-(triphenylsiloxy)-phenylarsine, a crystalline compound melting at 119-120°, was isolated from the reaction of sodium triphenylsilylanolate with diiodophenylarsine



A cyclic, dimeric species of composition $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$, was prepared by the condensation of diphenylsilylanediol with diiodophenylarsine in the presence of ammonia



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



It may be considered a dimer of the series $[-OSi(C_6H_5)_2OAsC_6H_5]_x$.

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.

(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.

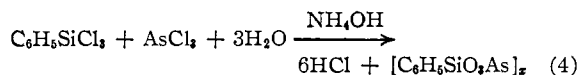
(2) Alfred P. Sloan Research Fellow.

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

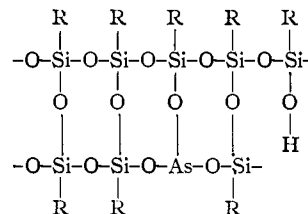
(4) M. Schmidt and H. Schmidbaur, *Angew. Chem.*, **71**, 553 (1959).

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 co-hydrolysis of arsenic trichloride with phenyltrichlorosilane. The proposed reaction is



The structure of the product, based on elemental analysis and infrared data, may be represented as shown below (where R is C_6H_5).



This material is analogous to a polymer containing Si-O-Al linkages reported by Andrianov, *et al.*,⁵ which had the approximate composition $[(C_6H_5SiO_{1.5})_3AlO_{1.5}H_2O]_x$.

The product obtained in the reaction expressed in equation 4 has the approximate composition $[(C_6H_5SiO_{1.5})_3AsO_{1.5}H]_x$. 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 $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$ 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-

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

TABLE II
 INFRARED SPECTRA OF NEW Si-O-As(III) DERIVATIVES

$[(C_6H_5)_3SiO]_2AsC_6H_5$ Wave no. (cm. ⁻¹)	$[(C_6H_5SiO)_2]_3$ $(AsO_{1.5}H)$ Wave no. (cm. ⁻¹)	$[-OSi(C_6H_5)_2OAs-$ $(C_6H_5)_2]$ Wave no. (cm. ⁻¹)	$[-OSi(C_6H_5)_2OAs-$ $(C_6H_5)_3]$ Wave no. (cm. ⁻¹)	Interpretation	Lit. Page no. ^a 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 H ₅	281
		1124(vs)	1124(vs)	Si-(C ₆ H ₅) ₂ doublet	^b
		1114(vs)	1114(vs)	Si-(C ₆ H ₅) ₂ doublet	^b
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 ₅	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. Servais, 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 (furthest 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 $C_6H_5As[OSi(C_6H_5)_2O]_2AsC_6H_5$ 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 $C_{64}H_{46}Si_3As_3O_6$: 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 ADI 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.