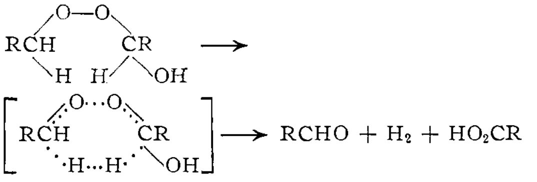
hydrogen is formed without hydrogen atoms.[27] They propose that bis-hydroxymethyl peroxide was the intermediate in this non-radical process. Since this was a gas phase reaction, a cage mechanism could not be involved. A concerted mechanism would explain these results in the gas phase as well as those in the present case in solution. Thus by analogy with this related reaction which does go in the gas phase, we may assume that the cage mechanism does not operate in the present reaction in solution. Furthermore, although a cage mechanism seems possible in an inert solvent, it hardly seems conceivable when the solvent is reactive towards the "caged" species as in the present case.

If in equation 4 the rate-determining step is $k_1$, then there would be no deuterium isotope effect when the corresponding deuterated compound was decomposed. As will be reported in the subsequent paper, there is such an isotope effect and thus this postulate is untenable. If one assumes that the recombination of the radicals within the cage to give starting material is such that the rate determining step is $k_3$, then an isotope effect would be anticipated. Under these circumstances one would expect the entropy of activation to be positive instead of negative as found.

The large negative entropy of activation (Table III) found is compatible with a rigid transition state and has been repeatedly found for reactions postulated to proceed from non-cyclic reactants *via* a cyclic transition state.[28]

Thus the cage mechanism is untenable and the evidence in favor of the cyclic concerted mechanism for the formation of hydrogen, acid and aldehyde from the hydroxybutyl butyl peroxide is substantial. The mechanism proposed (eq. 7) is compatible with all the data obtained so far. No other mechanism has been proposed which explains all of the facts.


(7)

**Acknowledgment.**—We wish to thank the National Science Foundation for financial support of this investigation.

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[27] D. W. G. Style and D. Summers, *Trans. Faraday Soc.*, **42**, 388 (1946).

[28] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 106; J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); E. G. Foster, A. C. Cope and F. Daniels, THIS JOURNAL, **69**, 1893 (1947); J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 24.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA]

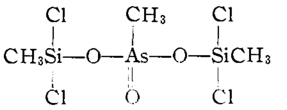
# Monomers and Polymers Containing Si–O–As Linkages[1]

BY BERTRAND L. CHAMBERLAND AND ALAN G. MACDIARMID

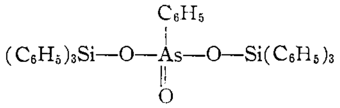
RECEIVED JANUARY 18, 1960

$[(C_6H_5)_3SiO]_3As$ was prepared by the interaction of $AsCl_3$ with $(C_6H_5)_3SiONa$ or with $(C_6H_5)_3SiOH$ in the presence of $NH_3$. It was also prepared by the cohydrolysis of $AsCl_3$ and $(C_6H_5)_3SiCl$. $[(C_6H_5)_3SiO]_3AsO$ was prepared by the reaction of $(C_6H_5)_3SiCl$ with $KH_2AsO_4$. The macro-molecular species, $(HO)_2As(O)[OSi(C_6H_5)_2OAs(O)OH]_2OH$ was prepared by the interaction of $(C_6H_5)_2SiCl_2$ with $KH_2AsO_4$ at room temperature. This product slowly decomposed to give a material whose composition approached $[OSi(C_6H_5)_2OAs(O)OH]_x$. $As[OSi(C_6H_5)_2O]_3As$ was prepared by the cohydrolysis of $AsCl_3$ and $(C_6H_5)_2SiCl_2$ and also by the interaction of $AsCl_3$ with $(C_6H_5)_2Si(OH)_2$ in the presence of either $(C_2H_5)_3N$ or $NH_3$. The physical, thermal and hydrolytic properties of the compounds prepared were examined.

Compounds of pentavalent arsenic containing Si–O–As linkages have been prepared by Kary and Frisch[2] by the interaction of both alkyl- and arylchlorosilanes with either alkyl- or aryl-arsonic acids to produce compounds such as


$$CH_3\underset{Cl}{\overset{Cl}{Si}}—O—\underset{\overset{\|}{O}}{\overset{CH_3}{As}}—O—\underset{Cl}{\overset{Cl}{Si}}CH_3$$

and


$$(C_6H_5)_3Si—O—\underset{\overset{\|}{O}}{\overset{C_6H_5}{As}}—O—Si(C_6H_5)_3$$

Hydrolysis of compounds of the above type did not proceed in a simple manner to give polymers containing alternating Si–O–As and O–Si–O linkages; instead, materials were obtained which had an arsenic to silicon ratio of only 1 to 12.

The present investigation was carried out for the purpose of preparing and characterizing monomers and polymers containing Si–O–As(III) or Si–O–As(V) linkages.

## Results and Discussion

Tris-(triphenylsilyl)-arsenite, $[(C_6H_5)_3SiO]_3As$, a colorless, microcrystalline substance melting at 190.5°, was prepared as indicated by the equations

$$AsCl_3 + 3(C_6H_5)_3SiOH + 3NH_3 \longrightarrow [(C_6H_5)_3SiO]_3As + 3NH_4Cl \quad (1)$$

$$AsCl_3 + 3(C_6H_5)_3SiONa \longrightarrow [(C_6H_5)_3SiO]_3As + 3NaCl \quad (2)$$

$$AsCl_3 + 3(C_6H_5)_3SiCl + 3H_2O \longrightarrow [(C_6H_5)_3SiO]_3As + 6HCl \quad (3)$$

Tris-(triphenylsilyl)-arsenate, $[(C_6H_5)_3SiO]_3AsO$, a colorless, crystalline substance melting at 240–

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[1] This report is based on portions of a thesis to be 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.

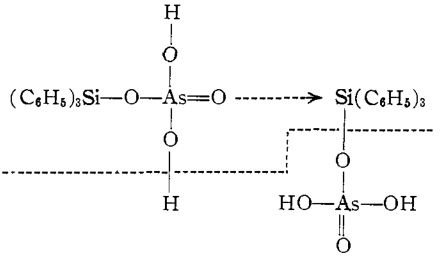
[2] (a) R. M. Kary and K. C. Frisch, THIS JOURNAL, **79**, 2140 (1957); (b) U. S. Patent 2,863,893 (1958).

242° was prepared by the interaction of an ethereal solution of $(C_6H_5)_3SiCl$ with either an excess or deficiency of $KH_2AsO_4$ at room temperature. The reaction proceeded fairly rapidly even though $KH_2AsO_4$ is insoluble in ether. The reaction appeared to have occurred in two stages, as indicated in equations 4 and 5, although the intermediate species could not be isolated.

$$KH_2AsO_4 + (C_6H_5)_3SiCl \longrightarrow (C_6H_5)_3SiOAs(O)(OH)_2 + KCl \quad (4)$$

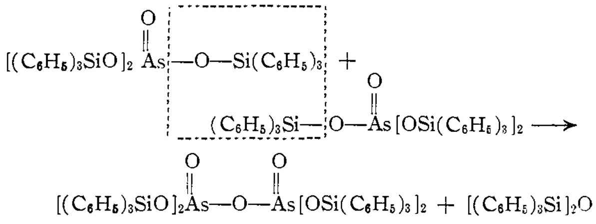
$$3(C_6H_5)_3SiOAs(O)(OH)_2 \longrightarrow [(C_6H_5)_3SiO]_3AsO + 2H_3AsO_4 \quad (5)$$

Condensation of the primary product apparently occurred in steps as indicated below to form tris-(triphenylsilyl)-arsenate as the end product.



The vacant 3d orbitals of the silicon could readily accept an electron pair from the As=O to form a linkage in an activated complex which could then decompose with the elimination of $H_3AsO_4$.

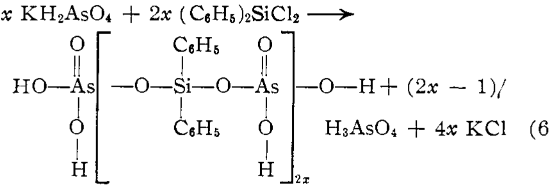
Tris-(triphenylsilyl)-arsenite distilled unchanged *in vacuo* at 351°; when heated at 420° for several hours decomposition occurred with the formation of a sticky material. Tris-(triphenylsilyl)-arsenate could not be distilled. Decomposition was rapid at 290° and after heating at 300–360° for several hours a sticky material was again obtained. The sticky material formed in both of the above cases might contain As–O–As linkages produced by the stepwise elimination of hexaphenyldisiloxane, *e.g.*



$$[(C_6H_5)_3SiO]_2\overset{O}{\overset{\|}{As}}{-}O{-}Si(C_6H_5)_3 + (C_6H_5)_3Si{-}O{-}\overset{O}{\overset{\|}{As}}[OSi(C_6H_5)_3]_2 \longrightarrow [(C_6H_5)_3SiO]_2\overset{O}{\overset{\|}{As}}{-}O{-}\overset{O}{\overset{\|}{As}}[OSi(C_6H_5)_3]_2 + [(C_6H_5)_3Si]_2O$$

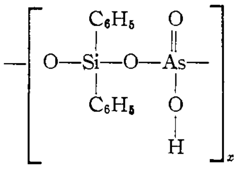
Both tris-(triphenylsilyl)-arsenite and tris-(triphenylsilyl)-arsenate were hydrolyzed only very slightly when dissolved in acetone–water solutions.

In an attempt to prepare a polymer containing alternating Si–O–As linkages, an ethereal solution of $(C_6H_5)_2SiCl_2$ was treated with excess $KH_2AsO_4$ at room temperature. The over-all reaction may be expressed by the equation



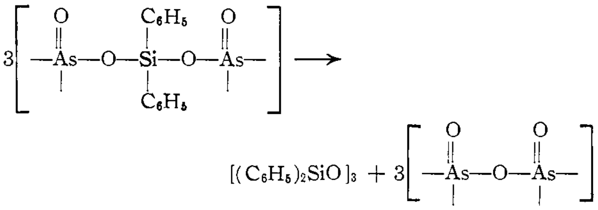
$$4x\ KH_2AsO_4 + 2x\ (C_6H_5)_2SiCl_2 \longrightarrow HO{-}\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{\underset{O}{\underset{|}{As}}}}}\left[{-}O{-}\overset{C_6H_5}{\overset{|}{\underset{\underset{C_6H_5}{|}}{Si}}}{-}O{-}\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{\underset{O}{\underset{|}{As}}}}}\right]_{2x}{-}O{-}H + (2x-1)/\ H_3AsO_4 + 4x\ KCl \quad (6)$$

On evaporation of most of the ether, a viscous sticky liquid was obtained, and complete removal of the ether gave a solid whose composition corresponded to the species given above where $x$ equals one. This substance hydrolyzes at a measurable rate. Above 120° it loses water and gives a glassy, resinous material. On standing, the viscous liquid described above slowly eliminated more $H_3AsO_4$ with a consequent increase in the value of $x$, to give polymers with composition approaching



$$\left[{-}O{-}\overset{C_6H_5}{\overset{|}{\underset{\underset{C_6H_5}{|}}{Si}}}{-}O{-}\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{\underset{O}{\underset{|}{As}}}}}{-}\right]_x$$

A little $[(C_6H_5)_2SiO]_3$ was also isolated in this reaction. This would indicate that a very small number of the Si–O–As linkages may have undergone reaction as



$$3\left[{-}\overset{O}{\overset{\|}{\underset{|}{As}}}{-}O{-}\overset{C_6H_5}{\overset{|}{\underset{\underset{C_6H_5}{|}}{Si}}}{-}O{-}\overset{O}{\overset{\|}{\underset{|}{As}}}{-}\right] \longrightarrow [(C_6H_5)_2SiO]_3 + 3\left[{-}\overset{O}{\overset{\|}{\underset{|}{As}}}{-}O{-}\overset{O}{\overset{\|}{\underset{|}{As}}}{-}\right]$$

This type of decomposition has previously been reported for other compounds containing Si–O–metal linkages.[3]

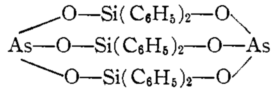
In another attempt to prepare polymeric species, the co-hydrolysis of $AsCl_3$ with $(C_6H_5)_2SiCl_2$ was investigated. The principal reaction occurring is

$$2AsCl_3 + 3(C_6H_5)_2SiCl_2 + 6H_2O \longrightarrow As[OSi(C_6H_5)_2O]_3As + 12HCl \quad (7)$$

The new compound, $As[OSi(C_6H_5)_2O]_3As$, was also prepared by the reaction of $AsCl_3$ with $(C_6H_5)_2Si(OH)_2$ in the presence of a hydrohalogen acceptor such as $NH_3$ or $(C_2H_5)_3N$. In both cases, reaction occurred as

$$2AsCl_3 + 3(C_6H_5)_2Si(OH)_2 \longrightarrow As[OSi(C_6H_5)_2O]_3As + 6HCl \quad (8)$$

The compound, $As[OSi(C_6H_5)_2O]_3As$, a white crystalline solid melting at 194–195°, has a molecular weight corresponding to the structure



It is, therefore, analogous to the antimony and boron compounds, $Sb[OSi(CH_3)_2O]_3Sb$[4] and $B[OSi(C_6H_5)_2O]_3B$.[5]

The compound $As[OSi(C_6H_5)_2O]_3As$ is not hydrolyzed to any measurable extent even in boiling acetone–water solutions. Instead, the melting point is lowered and it appears possible that the cyclic structure may be partly converted to a linear structure during this treatment.

In addition to the $As[OSi(C_6H_5)_2O]_3As$ produced according to equation 8, another substance, of

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(3) See P. E. Koenig, WADC Technical Report No. 58-160, 1958, p. 27.

(4) F. A. Henglein, R. Lang and K. Scheinost, *Makromol. Chem.*, **18**, 102 (1956).

(5) R. P. Anderson and M. M. Sprung, WADC Tech. Report, 59-61, March, 1959.

composition corresponding to $\text{As}[\text{OSi}(C_6H_5)_2\text{OSi}(C_6H_5)_2O]_3\text{As}$, (softens and melts, 35–50°) was isolated. This may be regarded as being derived from $\text{As}[\text{OSi}(C_6H_5)_2O]_3\text{As}$ as shown in equation 9. The wide melting point range and somewhat viscous solutions formed by this material suggests that it might contain linear as well as cyclic species.

$$2\text{As}[\text{OSi}(C_6H_5)_2O]_3\text{As} \longrightarrow \text{As}[\text{OSi}(C_6H_5)_2\text{OSi}(C_6H_5)_2O]_3\text{As} + \text{As}_2O_3 \quad (9)$$

## Experimental

**Reagents.**—Arsenic trichloride (Baker and Adamson reagent grade, b.p. 130–131°) was used without further purification. Anderson Chemical Company triphenylsilanol (98%) and triphenylchlorosilane (95–98%) and also Dow Corning Corp. purified diphenyldichlorosilane (95%) and diphenylsilanediol (99%) were used without further purification. Anhydrous diethyl ether, prepared by refluxing Mallinckrodt "anhydrous" ether (0.01% $H_2O$) with $LiAlH_4$ for several hours, followed by distillation, was used as the medium in most reactions. Fisher certified reagent grade benzene was treated with $LiAlH_4$, refluxed and then distilled for immediate use. Reagent grade, Matheson, Coleman and Bell potassium arsenate was used without further purification. Its composition was confirmed by analyzing for arsenic,[6] As found, 41.24, 41.80, calcd., for $KH_2AsO_4$, 41.61.

**TRIS-(TRIPHENYLSILYL)-ARSENITE. Preparation of $[(C_6H_5)_3\text{SiO}]_3\text{As}$. Method 1.**—Arsenic trichloride (1.81 g., 10.0 mmoles) in 50 ml. of dry benzene was added to triphenylsilanol (8.29 g., 30.0 mmoles), dissolved in 350 ml. of dry benzene in a three-necked, round-bottomed, one liter flask fitted with a mechanical stirrer, condenser with drying tube and gas inlet tube. After passing anhydrous ammonia through the solution for one hour, the mixture was refluxed for 20 minutes to remove excess ammonia.

The white precipitate which had formed weighed 2.00 g. and had a chloride content corresponding to 1.45 g. of $NH_4Cl$ (91% yield according to equation 1). On removing the benzene, first by distillation, and finally *in vacuo* at room temperature, crude $[(C_6H_5)_3\text{SiO}]_3\text{As}$ (5.6 g., m.p. 125–145°, 62% yield according to equation 1) remained. This product was washed several times with ether to obtain pure tris-(triphenylsilyl)-arsenite (m.p. 188–191°).

*Anal.*[7] Calcd. for $C_{54}H_{45}Si_3AsO_3$: C, 71.98; H, 5.04; Si, 9.34; As, 8.31. Found: C, 72.17; H, 5.29; Si, 9.53; As, 8.52.

Another experiment, using ether, gave 79% yields of both $NH_4Cl$ and crude product, which after purification yielded pure tris-(triphenylsilyl)-arsenite, (m.p. 189.5°, yield 39%).

**Method 2.**—The sodium salt of triphenylsilanol was prepared in 98% yields by refluxing an excess of sodium with triphenylsilanol (6.00 g., 21.7 mmoles) in 200 ml. of ether for 10 hr., followed by mechanical removal of the unreacted metal after a further 10 hr. at room temperature. Addition of 7.27 ml. of 0.923 M $AsCl_3$ in ether to the $(C_6H_5)_3\text{SiONa}$ immediately produced a fine white precipitate which was removed after refluxing for 1.5 hr. A chloride analysis on the precipitate indicated the presence of 0.97 g. (76% yield) of NaCl.

Upon complete removal of the ether from the filtrate the crude $[(C_6H_5)_3\text{SiO}]_3\text{As}$ obtained (3.23 g., 49% yield according to equation 2) was purified by washing several times with ether. The pure product (1.10 g., m.p. 189–190°) had an identical infrared spectrum to that of the product obtained by method 1.

*Anal.* Calcd. for $C_{54}H_{45}Si_3AsO_3$: C, 71.98; H, 5.04; Si, 9.34; As, 8.31. Found: C, 71.93; H, 5.17; Si, 9.56; As, 8.53.

**Method 3.**—Arsenic trichloride (1.81 g., 10.0 mmoles) in 50 ml. of benzene was slowly added during a period of thirty minutes, with constant stirring, to a mixture of triphenylchlorosilane (8.85 g., 30.0 mmoles) in 100 ml. of benzene and 9.18 ml. of ammonium hydroxide (30%, $d$ = 0.9016 g./ml.). After vigorous shaking for a further twenty minutes the white precipitate, which had formed, had absorbed all the excess water and was separated from the benzene solution by decantation.

Evaporation *in vacuo* of the filtered benzene decantate yielded a solid, which after washing with ether, was identified as pure tris-(triphenylsilyl)-arsenite (m.p. 190°; 4.5 g., 50% yield according to equation 3). Its infrared spectrum was identical to that of products prepared by methods 1 and 2.

The yields were found to vary considerably with slight variations in rate of addition of $AsCl_3$ and rate of stirring. The above yields were the highest obtained. More reproducible but smaller yields were obtained by adding the $NH_4OH$ to a mixture of the $AsCl_3$ and $(C_6H_5)_3\text{SiCl}$ in benzene. Tris-(triphenylsilyl)-arsenite is soluble in benzene and carbon tetrachloride, slightly soluble in acetone and ether and insoluble in methanol.

**Thermal Stability.**—Tris-(triphenylsilyl)-arsenite, (m.p. 188–191°) on heating *in vacuo*, with constant pumping, for 30 minutes at 351°, slowly distilled to the cooler (room temperature) end of the tube and solidified to a clear crystalline mass (m.p. 189–190°) which had an infrared spectrum identical to that of the starting material. No apparent decomposition occurred on heating the sample in an evacuated tube at 270° for one hour but when heated at 350° for a further three hours and then at 420° for three hours some decomposition was evident. The product obtained, a sticky material, still contained arsenic and was soluble in ether.

**Hydrolytic Stability.**—Tris-(triphenylsilyl)-arsenite (43.5 mg., m.p. 189.5–190.8°) was dissolved in 100 ml. of 10% water–acetone solution during 15 minutes and was then stirred continuously at room temperature for 90 minutes. As the compound dissolved, the relative *p*H (*p*H meter) decreased from 8.45 to 7.05 and during the next 70 minutes it decreased to 6.86. The solvent was removed *in vacuo* at room temperature and the recovered material melted at 185–187°.

**TRIS-(TRIPHENYLSILYL)-ARSENATE. Preparation of $[(C_6H_5)_3\text{SiO}]_3\text{AsO}$. Method 1. (Excess Triphenylchlorosilane).**—After stirring triphenylchlorosilane (10.0 g., 33.9 mmoles) in 100 ml. of ether with powdered $KH_2AsO_4$ (1.80 g., 9.95 mmoles) for 10 hr. at room temperature, the dense, ether-insoluble $KH_2AsO_4$ was replaced by a very fine white precipitate (7.11 g.). Upon removal of potassium chloride and $H_3AsO_4$ from this precipitate by extraction with methanol in a Soxhlet apparatus, the residue was washed with ether and was found to be pure $[(C_6H_5)_3\text{SiO}]_3\text{AsO}$ (m.p. 236–240°, 2.65 g., 87% yield according to equations 4 and 5—based on $KH_2AsO_4$ employed).

*Anal.* Calcd. for $C_{54}H_{45}Si_3AsO_4$: C, 70.71; H, 4.95; Si, 9.19; As, 8.17. Found: C, 70.44; H, 4.94; Si, 9.04; As, 7.92.

**Method 2. (Excess Potassium Dihydrogen Arsenate).**—After stirring triphenylchlorosilane (2.95 g., 10.0 mmoles) in 100 ml. of ether with powdered $KH_2AsO_4$ (3.60 g., 20.0 mmoles) for 7 hr. at room temperature, the insoluble material was removed by filtration. Analysis of the precipitate for chloride content indicated that the reaction had proceeded 43% towards completion. Upon standing for one half hour, the filtrate deposited short white needles on the walls of the container, which, after treatment with methanol as described in the previous experiment, were found to be pure $[(C_6H_5)_3\text{SiO}]_3\text{AsO}$, (m.p. 236–240°, 0.62 g., 20% yield according to equations 4 and 5—based on the $(C_6H_5)_3\text{SiCl}$ employed).

*Anal.* Calcd. for $C_{54}H_{45}Si_3AsO_4$: C, 70.71; H, 4.95; Si, 9.19; As, 8.17. Found: C, 70.61; H, 4.99; Si, 9.39; As, 7.99.

Since $[(C_6H_5)_3\text{SiO}]_3\text{AsO}$ is insoluble in both cold and hot ether, the crystallization of well-formed needles of the material from ether solution in this experiment suggests that the intermediate species, $(C_6H_5)_3\text{SiOAs(O)(OH)}_2$, may undergo slow decomposition on standing according to equation 5. On repeating the above experiments on several occasions, it was found that in each case where excess $KH_2AsO_4$ was used, the $[(C_6H_5)_3\text{SiO}]_3\text{AsO}$ crystallized in well-formed needles from the ether.

Tris-(triphenylsilyl)-arsenate is moderately soluble in benzene, carbon tetrachloride and acetone and insoluble in methanol and ether.

**Thermal Stability.**—Tris-(triphenylsilyl)-arsenate (m.p. 236–240°) on heating *in vacuo*, with continuous pumping for

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(6) H. H. Willard, N. H. Furman and C. E. Bricker, "Elements of Quantitative Analysis," D. van Nostrand Co., New York, N. Y., 1956, p. 259.

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

TABLE I

INFRARED SPECTRA

| $[(C_6H_5)_3SiO]_3As$ Wave no. (cm.$^{-1}$) | $[(C_6H_5)_3SiO]_3AsO$ Wave no. (cm.$^{-1}$) | $(HO)_2As(O)$-$[OSi(C_6H_5)_2OAs$-$(O)OH]_2OH$ Wave no. (cm.$^{-1}$) | $As[OSi(C_6H_5)_2O]_3$-As Wave no. (cm.$^{-1}$) | Interpretation | Ref. Page no.[a] |
|---|---|---|---|---|---|
| 3450(w) | 3448(w) | 3450(m) | 3420(vw) | | |
| 3080(m) | 3075(w) | 3080(s) | 3030(m) | =C—H stretch | 56 |
| 2325(vw) | 2325(vw) | 2330(m) | | | |
| 1968(w) | 1980(vw) | 1970(w) | 1962(w) | | |
| 1900(w) | 1905(vw) | 1902(w) | 1890(w) | | |
| 1830(w) | 1835(vw) | 1825(w) | 1820(w) | | |
| 1592(m) | 1592(w) | 1592(m) | 1591(m) | C=C ring stretch | 281 |
| 1490(m) | 1490(w) | 1490(w) | 1489(m) | C=C ring stretch | 281 |
| 1430(s) | 1430(s) | 1430(s) | 1430(s) | Si–$C_6H_5$(in solid) | 277–281 |
| 1335(w) | 1333(vw) | 1332(vw) | 1334(vw) | | |
| 1308(w) | 1308(vw) | 1308(vw) | 1305(w) | | |
| 1265(w) | 1265(vw) | 1265(w) | 1262(w) | | |
| 1187(m) | 1185(vw) | 1186(w) | 1186(m) | Si–$C_6H_5$ | 281 |
| | | | 1122(s) | $Si(C_6H_5)_2$ doublet | [b] |
| | | | 1113 (s) | $Si(C_6H_5)_2$ doublet | [b] |
| 1115(1108)(vs) | 1120(1106)(vs) | 1124(s) | | Si–$C_6H_5$ | 281 |
| 1028(w) | 1028(w) | 1042(m) | | Si–$C_6H_5$ | 281 |
| 1008(w) | 1008(m) | | 1008(s) | | |
| 998(m) | 998(m) | 998(w) | 998(s) | Si–$C_6H_5$ | 281 |
| | 975 (m) | | 975(w) | | |
| | 912(vs) | 912(s) | | Si—O—As=O (As V) | [c] |
| 882(vs) | | | 887(s) | Si-O-As (As III) | [c] |
| | | 808(s) | | | |
| 740(s) | 743(m) | 738(m) | 740(s) | Bending vib C-H | 277 |
| 711(vs) | 713(vs) | 713(s) | 717(s) | Out of plane C–H | 65 |
| 695(vs) | 698(vs) | 695(s) | 695(s) | 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, *et al.*, THIS JOURNAL, **70**, 3762 (1948). [c] The values of the Si–O–Si and Si–O–Ti stretching frequencies (V. A. Zeitler and C. A. Brown, *ibid.*, 61, 1174 (1957)) suggest that the Si–O–As stretch should appear in this region.

2 hr. at 290°, decomposed to give two crystalline bands (m.p. 142–144° and 142–194°) which formed in the cooler (room temperature) sections of the tube. Heating another sample in an evacuated tube at 225° for 45 minutes caused a darkening in color which did not increase appreciably after an additional hour at 275° and an hour at 300°. Further heating at 360° for 3.5 hr. produced a viscous liquid which flowed freely above 100°. After one hour at 400°, further decomposition was evident and on opening the tube a gaseous product and a very viscous dark mass were present.

**Hydrolytic Stability.**—Tris-(triphenylsilyl)-arsenate (141 mg., m.p. 238.5–239.8°) was dissolved in 100 ml. of 5% water–acetone solution during approximately 60 minutes and was then stirred continuously at room temperature for 30 minutes. As the compound dissolved, the relative *p*H (*p*H meter) decreased from 6.52 to 4.52 and during the next 30 minutes it decreased to 4.18. The solvent was removed *in vacuo* at room temperature and the recovered material melted at 237.5–240.0°.

**$(HO)_2As(O)[OSi(C_6H_5)_2OAs(O)OH]_2OH$. Preparation.**—After stirring a mixture of $KH_2AsO_4$, (24.8 g., 138 mmoles, 50% excess over that required by equation 6), with $(C_6H_5)_2SiCl_2$, (11.6 g., 45.8 mmoles), dissolved in 200 ml. of ether for 101 hr. at room temperature, the insoluble matter was removed by filtration. This contained 99% of the KCl and 96% of the arsenic acid required by eqation 6. On slow evaporation of the filtrate, crystallization of slightly impure $[(C_6H_5)_2SiO]_3$, (0.44 g., m.p. found, 182–184°, literature[8] 190°; confirmed by infrared spectrum[9]) occurred. Further evaporation yielded a clear viscous sticky liquid which deposited a tough resinous film on a glass surface and which formed a foam-like solid on complete removal of the ether *in vacuo*. Analysis was performed on a sample of the solid dried *in vacuo* in an Abderhalden apparatus at 80° for 1 hr.

*Anal.* Calcd. for $C_{24}H_{25}Si_2As_3O_{12}$: C, 36.66; H, 3.20; Si, 7.14; As, 28.58. Found: C, 36.95; H, 3.57; Si, 7.31; As, 28.24.

It was not possible to determine the molecular weight of this compound since it apparently decomposed on drying and was then only partially soluble in benzene, a white powder remaining undissolved. The substance softened and melted in the region of 125° to give a material which was a colorless resinous solid when cooled and decomposed rapidly at 200–250° with elimination of water.

After standing for several days the clear viscous liquid changed slowly to an opaque, white grease which was only partly soluble in ether. Upon addition of pentane to an ether extract of this grease, a white precipitate was formed, which after drying at 80° *in vacuo* was found to have a composition approaching $[-O(C_6H_5)_2Si-O-As(O)(OH)-]$. It melted in the range 153–180°.

*Anal.* Calcd. for $C_{12}H_{11}SiAsO_4$: C, 44.72; H, 3.44; Si, 8.72; As, 23.25. Found: C, 41.19; H, 4.84; Si, 10.26; As, 24.40.

**Hydrolytic Stability.**—Two weighed films of the original compound, prepared by evaporation of ethereal solutions of the substance, were covered with water for a total of 64 hr. during which time the water was periodically removed and was shown to contain arsenic acid. The films were dried at 100° and weighed before adding more water. After this treatment both films showed a 48–49% loss in weight and the arsenic content of the film remaining was approximately 18% that of the original compound.

**$As[OSi(C_6H_5)_2O]_3As$. Preparation. Method 1.**—A mixture of 3.20 g. of distilled water and 15.0 ml. of 30% $NH_4OH$ was slowly added to a solution of $AsCl_3$ (11.4 g., 62.6 mmoles) and diphenyldichlorosilane (16.4 g., 64.8 mmoles) in 300 mls. of benzene with constant stirring during a period of 20 minutes, and the mixture was then shaken vigorously for 20 minutes. The white, benzene-insoluble material (16.7 g.) which had formed absorbed all excess water and after separation by filtration was found to contain 1.7 g. of $As_2O_3$ and

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(8) C. A. Burkhard, THIS JOURNAL, **67**, 2173 (1945).

(9) C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

water-soluble chloride. Partial evaporation of the filtrate *in vacuo* at room temperature yielded a solid which after several washings with ether, was identified as pure crystalline $As[OSi(C_6H_5)_2O]_3As$ (m.p. 195°, 3.0 g., 40% yield according to equation 7).

*Anal.* Calcd. for $C_{36}H_{30}As_2Si_3O_6$: C, 54.54; H, 3.82; Si, 10.63; As, 18.90. Found: C, 54.30; H, 3.82; Si, 10.77; As, 18.62.

Cryoscopic measurements in benzene gave a molecular weight of 782, calcd. for $As[OSi(C_6H_5)_2O]_3As$, 793. It is soluble in benzene and chloroform and moderately soluble in acetone and ether.

Complete evaporation of the solvent yielded a very viscous liquid containing silicon and arsenic in a ratio of 10 to 1.

**Method 2.**—An ethereal solution of $AsCl_3$ (1.09 g., 6.02 mmoles) in 25 ml. of ether was added to a solution of diphenylsilanediol (1.95 g., 9.01 mmoles) in 100 ml. of ether. The white precipitate (2.59 g.) which formed immediately upon addition of triethylamine (1.82 g., 18.0 mmoles) to this solution was identified as $(C_2H_5)_3N\cdot HCl$ (m.p., found, 255°, literature,[10] 253–254°; positive test for chloride in aqueous solution) and corresponded to a 95% yield of HCl according to equation 8.

On partial evaporation, the filtrate yielded crystalline $As[OSi(C_6H_5)_2O]_3As$, (m.p. 194°; mol. wt. found, 785, calcd., 793; infrared spectrum identical to that of product obtained by method 1; 0.99 g., 42% yield according to equation 8).

Further evaporation of the ether yielded a viscous liquid which formed a fluffy solid (1.32 g.) upon complete removal of the solvent *in vacuo*. After redissolving in ether, removal of a small quantity of insoluble material by filtration, followed by re-evaporation, $As[OSi(C_6H_5)_2OSi(C_6H_5)_2O]_3As$ (m.p. 35–50°), a material very soluble in benzene, chloroform, ether and acetone, was obtained.

*Anal.* Calcd. for $C_{72}H_{60}Si_6As_2O_9$: C, 62.29; H, 4.36; S, 12.14; As, 10.79. Found: C, 63.77; H, 4.60; Si, 12.20; As, 11.39.

**Method 3.**—Anhydrous ammonia was bubbled through a solution of $AsCl_3$ (1.09 g., 6.02 mmoles) and diphenylsilanediol (1.95 g., 9.01 mmoles) in 100 ml. of ether for ten minutes, and after standing for 20 minutes the precipitated $NH_4Cl$ was removed by filtration and was found to have a chloride content corresponding to an 82% yield of HCl according to equation 8.

Slow evaporation of the filtrate first deposited a small quantity of $As_2O_3$ and then yielded crystalline $As[OSi(C_6H_5)_2O]_3As$ (m.p. 194°; mol. wt. found, 797, calcd., 793; infrared spectrum identical to that of the product obtained by method 1; 0.60 g., 30% yield according to equation 8). Complete evaporation of the filtrate yielded a small amount of sticky, viscous liquid.

**Hydrolytic Stability.**—After adding 5 ml. of distilled water to a solution of $As[OSi(C_6H_5)_2O]_3As$ (98.9 mg., m.p. 194°) in 95 ml. of acetone, the clear solution was stirred for 90 minutes at room temperature and the solvent was then removed *in vacuo* at room temperature. The residue had the same weight as the original sample and melted at 176–180°; it did not crystallize on cooling to room temperature but formed a hard glass.

In another experiment, a solution of 113.6 mg. of the compound in 100 ml. of 95% acetone–water mixture was stirred for 90 minutes at room temperature, and after removal of the solvent by boiling for 30 minutes, the sample was found to have increased in weight by only 1.6 mg. and melted in the range 140–143°.

**Infrared Spectra.**—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 2–3 mg. of compound per 300 mg. of KBr.

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[10] Lange's, "Handbook of Chemistry", 8th Ed., Handbook Publishers, Inc. (1952).