Anal. Calcd. for $C_6H_{10}OSn$: Sn, 54.75. Found: Sn, 54.11.

Similarly divinyltin oxide (42%) has been prepared from divinyltin dichloride and aqueous sodium hydroxide.

Anal. Calcd. for C_4H_6OSn: Sn, 62.95. Found: Sn, 62.60.

Acknowledgments.—The authors wish to thank Dr. Marie Farnsworth and her co-workers in the Physical and Analytical Section of this Laboratory for their assistance throughout this work.

RAHWAY, NEW JERSEY

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES OF THE AMERICAN SMELTING AND REFINING COMPANY AND THE RESEARCH LABORATORIES OF E. F. HOUGHTON & CO.]

Arsonosiloxanes[1]

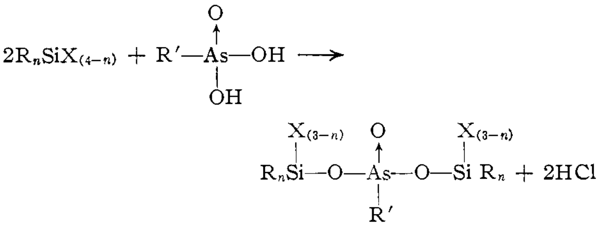
BY ROLAND M. KARY AND KURT C. FRISCH

RECEIVED APRIL 25, 1956

The well-known silicones, such as polymethylsiloxanes, do not exhibit pesticidal properties. Organic arsenical siloxanes could be used to control pest organism in addition to already existing utilities of conventional silicones. It was found that arsenic can be incorporated into siloxane structures by formation of Si–O–As bonds from a novel reaction between organic chlorosilanes and organic arsonic acids. Formation of arsonosiloxane polymers from hydrolysis of chlorosilylarsonates appears to be feasible. Methyl- and phenylchlorosilylarsonates were synthesized and hydrolyzed to the corresponding arsenical siloxane derivatives. Compounds found were identified by chemical analysis and infrared absorption characteristics.

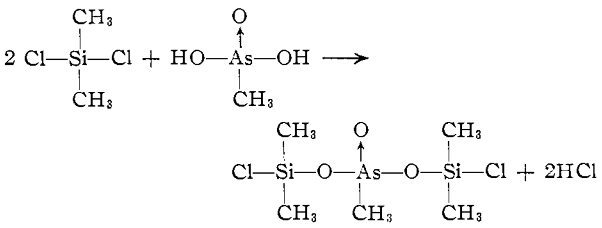
The well-known utilities of silicones, particularly of methylsilicones, do not include action toward pest organisms. Organic arsenical siloxane derivatives could conceivably exhibit pesticidal properties which would add numerous possibilities of applications to those already existing. Therefore, the investigation of organic arsenical silanes and siloxane derivatives was undertaken in order to prepare compounds containing Si–O–As bonds. It was found that methyl- and phenylchlorosilanes react with methyl- and phenylarsonic acids in the presence of an inert solvent such as benzene or carbon tetrachloride, at the temperature of 80° at which these solvents are kept refluxing for about 24 hr. under agitation.

As is shown by the following equation, 2 moles of chlorosilane react with one mole arsonic acid to form a "bis" or neutral chlorosilylarsonate and 2 moles of hydrochloric acid



$$2\mathrm{R}_n\mathrm{SiX}_{(4-n)} + \mathrm{R'}-\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{As}}}-\mathrm{OH} \longrightarrow \mathrm{R}_n\overset{\overset{\mathrm{X}_{(3-n)}}{|}}{\mathrm{Si}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{R'}}{|}}{\mathrm{As}}}-\mathrm{O}-\overset{\overset{\mathrm{X}_{(3-n)}}{|}}{\mathrm{Si}}\,\mathrm{R}_n + 2\mathrm{HCl}$$

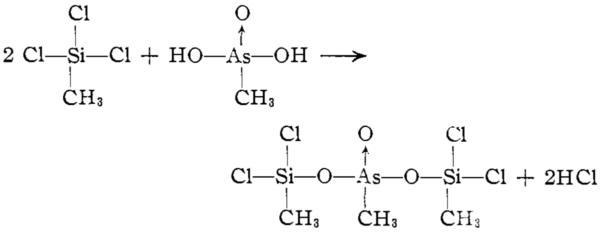
Thus, the reaction between dimethyldichlorosilane and methylarsonic acid resulted in bis-(dimethylchlorosilyl)-methylarsonate (I), shown by the equation



$$2\,\mathrm{Cl}-\overset{\overset{\mathrm{CH_3}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{Cl} + \mathrm{HO}-\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{As}}}-\mathrm{OH} \longrightarrow \mathrm{Cl}-\overset{\overset{\mathrm{CH_3}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{As}}}-\mathrm{O}-\overset{\overset{\mathrm{CH_3}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{Cl} + 2\mathrm{HCl}$$

I

In similar manner, bis-(methyldichlorosilyl)-methylarsonate (II) was prepared from methyltrichlorosilane and methylarsonic acid

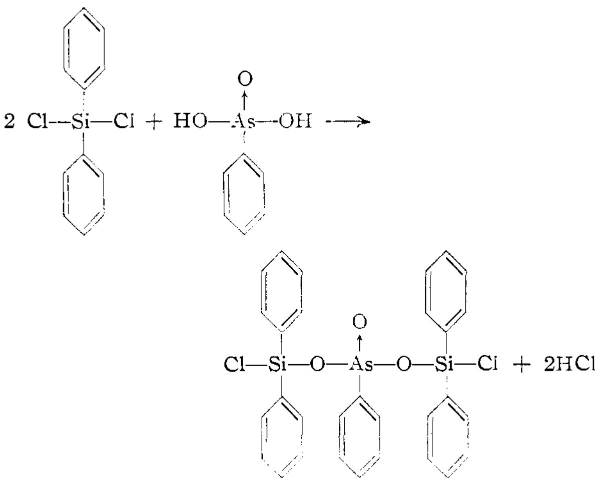


$$2\,\mathrm{Cl}-\overset{\overset{\mathrm{Cl}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{Cl} + \mathrm{HO}-\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{As}}}-\mathrm{OH} \longrightarrow \mathrm{Cl}-\overset{\overset{\mathrm{Cl}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{As}}}-\mathrm{O}-\overset{\overset{\mathrm{Cl}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{Cl} + 2\mathrm{HCl}$$

II

These reactions were carried out in 2:1 molar ratio of chlorosilane and methylarsonic acid. If a 1:1 molar ratio was employed, poor yields of the "bis" compounds were obtained, together with considerable amounts of unreacted starting materials.

Essentially, the same method was used to prepare the corresponding phenyl derivatives. Bis-(diphenylchlorosilyl)-phenylarsonate (III) was synthesized from diphenyldichlorosilane and phenyl arsonic acid



III

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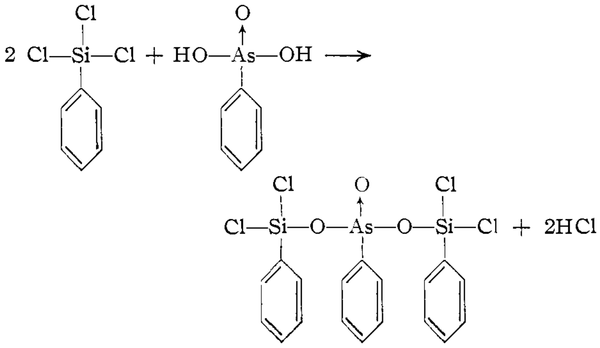
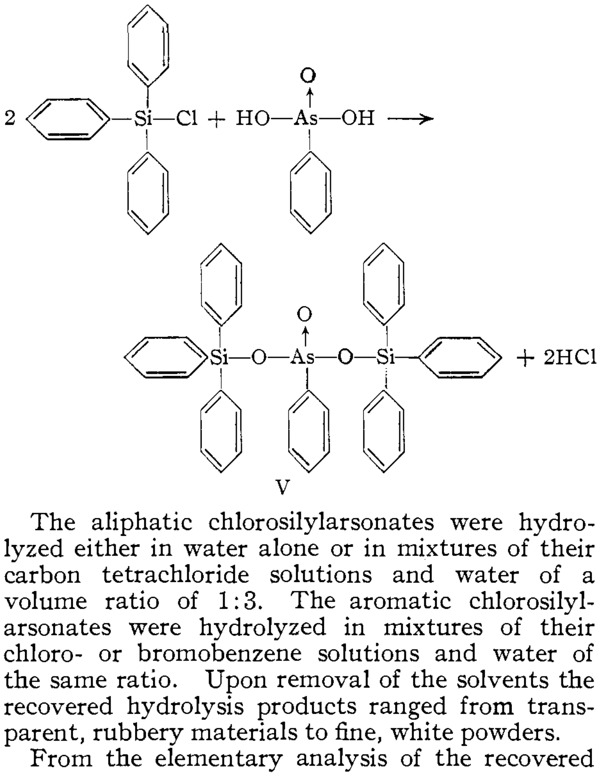
[1] Presented at the 129th Meeting of The American Chemical Society, Dallas, Texas.

Similarly, bis-(phenyldichlorosilyl)-phenylarsonate (IV) was made, using phenyltrichlorosilane and phenylarsonic acid



IV

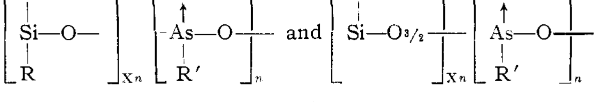
Bis-(triphenylsilyl)-phenylarsonate (V) was synthesized by treating triphenylchlorosilane with phenylarsonic acid, using pyridine as a hydrohalogen acceptor



V

The aliphatic chlorosilylarsonates were hydrolyzed either in water alone or in mixtures of their carbon tetrachloride solutions and water of a volume ratio of 1:3. The aromatic chlorosilylarsonates were hydrolyzed in mixtures of their chloro- or bromobenzene solutions and water of the same ratio. Upon removal of the solvents the recovered hydrolysis products ranged from transparent, rubbery materials to fine, white powders.

From the elementary analysis of the recovered products, it became apparent that some cleavage of the Si–O–As bond had taken place as could be expected from theoretical considerations. However, the resulting hydrolysis products still contained both arsenic and silicon, even after repeated washing with water, and appeared to be copolymers of the general formulas:



$$\left[\begin{array}{c}R\\|\\Si—O—\\|\\R\end{array}\right]_{xn}\left[\begin{array}{c}O\\\uparrow\\-As—O—\\|\\R'\end{array}\right]_{n} \text{ and } \left[\begin{array}{c}R\\|\\Si—O_{3/2}—\\ \\ \end{array}\right]_{xn}\left[\begin{array}{c}O\\\uparrow\\As—O—\\|\\R'\end{array}\right]_{n}$$

Infrared data on some of the above compounds lend additional evidence to the postulated structures.

Experimental

Methylarsonic Acid.—Methylarsonic acid was obtained as its disodium salt, according to Meyer's reaction from sodium arsenite and methyl chloride.[2] The free acid was isolated through the calcium salt by decomposition of the latter with sulfuric acid, followed by precipitation upon concentrating the filtrate (from $CaSO_4$), and recrystallization from ethanol.

Phenylarsonic Acid.—Phenylarsonic acid was used as the available "D.P.I.—Eastman Kodak—Benzenearsonic Acid" without further purification.

Methyl- and Phenylchlorosilanes.—The methyl- and phenylchlorosilanes were used as the available Linde Air Products or General Electric Co. preparations without further purification.

Bis-(dimethylchlorosilyl)-methylarsonate (I).—Seventy g. (0.5 mole) of methylarsonic acid was suspended in 400 ml. of dry benzene by stirring at room temperature. One hundred and twenty-nine g. of dichlorodimethylsilane was added slowly from a separatory funnel, so as to keep the ensuing exothermic increase in temperature to a minimum of 10–15°. After the initial reaction, indicated by a considerable evolution of HCl gas, had abated, the mixture was refluxed for 24 hr., under a drying tube containing "Drierite." Upon cooling to room temperature, the amount of unreacted methylarsonic acid, which is practically insoluble in benzene, was found to be 8%. It was subsequently removed by filtration.

After removal of the solvent under atmospheric and reduced pressure, 111 g. of I or 68% was obtained in form of a pale-yellow oil.

Anal. Calcd. for $C_6H_{15}O_3Cl_2Si_2As$: Si, 17.3; As, 23.1; Cl, 21.8; C, 17.8; H, 4.6. Found: Si, 17.4; As, 22.7; Cl, 21.9; C, 18.5; H, 5.4.

Bis-(methyldichlorosilyl)-methylarsonate (II).—Seventy g. (0.5 mole) of methylarsonic acid reacted with 150 g. (1.0 mole) of methyltrichlorosilane in the same manner as described before.

Removal of the solvent yielded II, a resinous, somewhat transparent solid. The yield was 154 g., corresponding to 84% of the theoretical. Since the purification of this material proved to be extremely difficult, the resulting product was hydrolyzed directly to the corresponding polymer VII.

Bis-(diphenylchlorosilyl)-phenylarsonate (III).—Twenty and two-tenths g. (0.1 mole) of phenylarsonic acid reacted in the same manner as described before with 50.6 g. (0.2 mole) of diphenyldichlorosilane resulting in formation of III as a white, amorphous solid. The yield was 51 g. or 80% of the theoretical.

Anal. Calcd. for $C_{30}H_{25}O_3Cl_2Si_2As$: Si, 8.8; As, 11.8; Cl, 11.2; C, 56.7; H, 4.0. Found: Si, 8.6; As, 11.8; Cl, 11.0; C, 57.0; H, 4.7.

Bis-(phenyldichlorosilyl)-phenylarsonate (IV).—Twenty and two-tenths g. (0.1 mole) of phenylarsonic acid reacted in the same manner as described before with 42.3 g. (0.2 mole) of phenyltrichlorosilane which resulted in formation of IV as a somewhat resinous, amorphous solid. The yield was 43 g. or 78.2% of the theoretical.

Here, again, purification of the resulting dichlorosilyl derivative presented some serious obstacles, and the product was hydrolyzed directly to the corresponding polymer.

Bis-(triphenylsilyl)-phenylarsonate (V).—Twenty and two-tenths g. (0.1 mole) of phenylarsonic acid was suspended in 400 ml. of dry benzene containing 79.1 g. of pyridine which latter is an excess over the theoretically required 15.8 g. (0.2 mole). To this mixture 59.0 g. (0.2 mole) of triphenylchlorosilane dissolved in 400 ml. of dry benzene was added gradually. The formation of a precipitate accompanied by an exothermic temperature increase of 7° was observed. The mixture was then heated to reflux (80–82°) which was maintained for 24 hr. After cooling to room temperature, the precipitate was filtered off and dried. It consisted almost entirely of pyridine monohydrochloride. The filtrate was subjected to solvent removal under atmospheric and reduced pressure upon which 66.5 g. or 92.6% was recovered as a white, waxy solid.

Anal. Calcd. for $C_{42}H_{35}O_3Si_2As$: Si, 7.8; As, 10.4; C, 70.3; H, 4.9. Found: Si, 7.0; As, 10.3; C, 69.6; H, 4.3.

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[2] G. Meyer, *Ber.*, **16**, 1440 (1883); G. E. Miller and S. G. Seaton, U. S. Patent 2,442,372 (1948); *C. A.*, **42**, 6842 (1948); U. S. Patent 2,695,306 (1954).

Polymethylarsonodimethylsiloxane (VI).—Ten g. of bis-(dimethylchlorosilyl)-methylarsonate was dissolved in 100 ml. of carbon tetrachloride and added gradually from a separatory funnel through a tube reaching into 100 ml. of CCl_4 agitated with 300 ml. of water, at about 40–50°, during 25–35 minutes. After cooling to room temperature and subsequent washing with water to remove hydrochloric acid found during hydrolysis, the CCl_4 (bottom) layer was drawn off, dried over anhydrous Na_2SO_4 and the solvent removed under atmospheric and reduced pressure. Three and six-tenths g. of VI, a translucent, rubbery material was obtained.

Anal. Calcd. for $C_{25}H_{75}O_{14}Si_{12}As$: Si, 33.3; As, 7.4; C, 29.7; H, 7.4. Found: Si, 33.6; As, 7.7; C, 29.8; H, 8.1.

Polymethylarsonomethylsiloxane (VII).—One hundred and nine g. of bis-(methyldichlorosilyl)-methylarsonate was leached with boiling water for about 1 hr., washed thoroughly with water of room temperature, filtered off and dried. Forty-five g. of VII, a fine white powder, was obtained.

Anal. Calcd. for $C_{13}H_{39}O_{20}Si_{12}As$: Si, 36.3; As, 8.1; C, 15.5; H, 3.9. Found: Si, 37.1; As, 7.5; C, 15.8; H, 4.6.

The above VI and VII thus appear to be copolymers of the previously given formula where X is about 12.

The aromatic chlorosilylarsonates were found to be soluble in bromobenzene which is a suitable solvent for this type of controlled hydrolysis.[3] Essentially, the same method of hydrolysis was performed as described before. So far only impure polymers have been obtained as the result of this hydrolysis. The infrared data were obtained by means of a Perkin–Elmer Double Beam Recording Infrared Spectrophotometer, Model 21. Data on infrared absorption maxima, characteristic for regular siloxane compounds, were available from the literature.[4] Unpublished data on infrared absorption maxima, characteristic for organoarsenic compounds, were available from known or novel organic arsenicals, such as methylarsonic acid, arsenomethane As-1,2-disulfide[5] and others. Compound I was examined as liquid film in capillary thickness, whereas compound VII had to be used as 2% solution in chloroform. Polydimethylsiloxane, General Electric Co.—SF-96 (300), was used as a standard reference.

INFRARED ABSORPTION CHARACTERISTICS[6]

Compound	Microns	Intensity	Assignment
Bis-(dimethylchlorosilyl) methylarsonate	3.40	Strong	C–H stretching (for $Si-CH_3$)
	5.10	Strong	
	5.50	Strong	
	6.20	Weak	As=O (As → O)
	6.75	Strong	As–C
	7.10	Strong	C–H bending
	7.95	Strong	$Si-CH_3$ rocking
	9.5	Strong, broad	Si–O stretching
	10.8	Strong, broad	
	11.6	Strong, broad	Si–C stretching
Polymethylarsonodimethylsiloxane	3.40	Strong	C–H stretching (for $Si-CH_3$)
	5.10	Weak	
	6.20	Strong	As=O (As → O)
	6.75	Weak	As–C
	7.15	Strong	C–H bending
	7.95	Strong	$Si-CH_3$ rocking
	9.50	Strong, broad	Si–O stretching
	11.65	Strong, broad	Si–C stretching
Polydimethylsiloxane	3.40	Strong	C–H stretching (for $Si-CH_3$)
	7.10	Medium	C–H bending
	7.95	Strong	$Si-CH_3$ rocking
	9.50	Strong, broad	Si–O stretching
	11.60	Medium	Si–C stretching
	12.50	Strong, broad	

Acknowledgments.—The authors wish to express their appreciation to Dr. P. A. van der Meulen and M. F. Borek of Rutgers University Chemistry Department for the infrared data and to Messrs. W. E. Bell and K. C. Braun for their assistance in the Experimental part reported in this paper.

PLAINFIELD, NEW JERSEY

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[3] C. E. Welsh and N. G. Holdstock, U. S. Patent 2,661,348 (1953); *C. A.*, **48**, 3063 (1954).

[4] N. Wright and M. J. Hunter, THIS JOURNAL, **69**, 803 (1947).

[5] R. M. Kary, U. S. Patent 2,646,440 (1953).

[6] Material supplementary to this article has been deposited as Document number 5076 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.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Kinetics of the Hydrolysis of Acetylenic Chlorides and Their Reactions with Primary and Secondary Aliphatic Amines[1]

BY G. F. HENNION AND KENNETH W. NELSON[2]

RECEIVED NOVEMBER 30, 1956

Acetylenic chlorides of the type RR'C(Cl)—C≡CH undergo very slow solvolysis in 80% ethanol at 25°. The rate is accelerated by addition of sodium hydroxide, and the reactions then commonly follow second-order kinetics. Primary and secondary aliphatic amines are smoothly alkylated by these halides. The mechanisms of these reactions are discussed.

Discussion

It was reported in a previous paper[3] in this series that 3-chloro-3-methyl-1-butyne undergoes extremely slow solvolysis in 80% ethanol at 25° (k_1 = 7.4 × 10^{-4} hr.$^{-1}$). This was attributed to lack of steric strain, despite the tertiary structure, and the inductive (electron-withdrawing) effect of the ethynyl group. Burawoy and Spinner[4] have verified these findings (k_1 said to be 8.48 × 10^{-4} hr.$^{-1}$) in a recent study of the behavior of alkylethynyldimethylcarbinyl chlorides. It is interesting to note from the latter work that when the ethynyl hydrogen atom is replaced by an alkyl group, the rate of solvolysis is increased by a factor of 1000. In the presence of dissolved alkali, 3-chloro-3-methyl-1-butyne reacts by second-order

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[1] Paper LXIV on substituted acetylenes; previous paper, *J. Org. Chem.*, **21**, 1142 (1956).

[2] Miles Laboratories Fellow, 1954–1955; Reilly Fellow, 1955–1956. Abstracted from the Ph.D. Dissertation of K. W. N., 1956.

[3] G. F. Hennion and D. E. Maloney, THIS JOURNAL, **73**, 4735 (1951).

[4] A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).