polymers will be the subject of a future publication.

Experimental

Oxidation of 1-Ethynylcyclohexanol. General Procedure.—To a 250-ml. wide-mouthed Erlenmeyer flask in a water bath at 28° was added 135 ml. of acetone, 1 g. (0.01 mole) of copper(I) chloride and 1.2 g. (0.01 mole) of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine. Oxygen was bubbled into the solution which was vigorously stirred by means of a "Vibromixer" stirrer. Over a 15-min. period, 25 g. (0.20 mole) of 1-ethynylcyclohexanol was added in a dropwise manner to the reaction mixture. The temperature rapidly rose to 42°. After the addition was complete, the reaction was continued for 20 min., then the acetone was evaporated and there was added 20 ml. of water containing 1 ml. of concentrated hydrochloric acid. The colorless solid was filtered in a Büchner funnel, washed with a small amount of water, and dried *in vacuo*. There was obtained 22.9 g. (0.093 mole, 93% yield) of 1,1'-butadiynylenedicyclohexanol,[5] m.p. 177° (lit. 173–174°).

The following acetylenes were oxidized in an identical fashion (yield of the coupled product and melting point of the coupled product in brackets): phenylacetylene (97.0%, 87–88°); 3-hydroxy-3-methyl-1-butyne (85.0%, 138°); 3-hydroxy-3-methyl-1-pentyne (82.3%, 93–95°); 1-ethynylcyclopentanol (89.5%, 138–140°).

Determination of Rates.—The quantitative rate experiments were performed in a 100-ml. reactor equipped with an oxygen inlet tube, vibromixer stirrer, and a dropping funnel in a water bath at 30°. Oxygen was supplied to the reactor at atmospheric pressure by means of a 100-ml. gas burette and leveling bulb. The catalyst was preoxidized and when the system reached equilibrium the acetylene was added and the progress of the reaction was followed by the change in volume in the gas burette. Table I outlines the experiments.

TABLE I

[Cu] (M × 10^{-3})	RC≡CH[a]	$t_{1/2}$ (min.) A[b]	B	C
5	Phenylacetylene	270	96	10[c]
15	1-Ethynylcyclohexanol	420	360	13
60	Hexyne-1	550	950	55

[a] The concentration of the acetylene in all cases is 0.4 *M* and all the reactions were run at 30°. [b] In A the catalyst is copper(II) acetate hydrate in pyridine solvent; B is copper(I) chloride in pyridine solvent; C is copper(I) chloride plus an equivalent amount (moles) of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine in isopropyl alcohol solvent. Acetone, which was used in the larger scale preparative examples, could not be used here because of its high vapor pressure at 30°. The half-times were reproducible within ±3%. [c] In this example Methyl Cellosolve was the solvent. When isopropyl alcohol was used, some phenylethynylcopper(I) deposited giving erratic results.

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Systems Containing a Silicon–Oxygen–Vanadium Linkage[1]

M. M. CHAMBERLAIN, G. A. JABS,
AND B. B. WAYLAND[2]

Morley Chemical Laboratory,
Western Reserve University, Cleveland 6, Ohio

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In 1958 Orlov, *et al.*,[3] reported the preparation of tris(triphenylsilyl)vanadate(V) by reaction of tris(*n*-butoxy)vanadate(V) and triphenylsilanol. Cohen and Dessy[4] have reported the preparation of tetrakis(triphenylsiloxy)vanadium(IV) by reaction of sodium triphenysilanolate and vanadium(IV) chloride. As part of our work in the preparation of inorganic macromolecules containing a silicon–oxygen–metal linkage, we have developed new methods for the preparation of tris(triphenylsilyl) vanadate(V) and have modified the reported methods to give high yields of the vanadium(IV) product. Further, we have prepared the previously unreported compound tris(triphenylsilyl)thiovanadate(V) and have developed a quick and accurate method for the quantitative determination of silicon and vanadium in these esters.

Experimental

Preparation of Tetrakis(triphenylsiloxy)vanadium(IV).—Tetrakis(triphenylsiloxy)vanadium(IV) was prepared by the reaction of sodium triphenylsilanolate and vanadium(IV) chloride in anhydrous benzene.

In a typical preparation 10.2 g. (0.037 mole) of triphenylsilanol was dissolved in 100 ml. of anhydrous benzene and an excess of clean metallic sodium added. The reaction mixture was stirred for 5 hr. at room temperature, the unchanged sodium metal separated, and the solution of sodium triphenylsilanolate used immediately.

The vanadium(IV) chloride was prepared by the reaction of ferrovanadium (74% vanadium content) and chlorine gas at 350° in a tube furnace. The crude vanadium(IV) chloride was purified by distillation and the portion boiling 147–148° at 1 atm. pressure used (lit., b.p. 147.5°).

One milliliter (0.094 mole) of the purified vanadium(IV) chloride was dissolved in 75 ml. of anhydrous benzene and added slowly with vigorous stirring to the freshly prepared solution of sodium triphenylsilanolate. The reaction mixture was kept at 15° with an ice bath and protected at all times by a blanket of dry nitrogen or natural gas. A purple precipitate formed immediately.

After addition of the vanadium(IV) chloride solution, the reaction mixture was stirred vigorously for a few minutes and the mixture of tetrakis(triphenylsiloxy)vanadium(IV) and sodium chloride removed by filtration. The filter cake was washed, first with cold water until no trace of chloride ion appeared in the wash water, then with benzene to remove traces of triphenylsilanol and the by-product tris(tri-

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(1) This work has been supported in part by the Office of Naval Research.

(2) Present address: University of Illinois, Urbana, Illinois.

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phenylsilyl)vanadate(V). A final washing with cold diethyl ether removes traces of hexaphenyldisiloxane.

Tetrakis(triphenylsiloxy)vanadium, prepared in this fashion, was a pale blue-green solid melting at 264–268°.

Yield is 63% based upon triphenylsilanol when nitrogen is used as an inert atmosphere and 86% when natural gas is used as a reducing atmosphere.

Anal. Calcd. for $[(C_6H_5)_3SiO]_4V$: C, 75.06; H, 5.25; V, 4.42; Si, 9.75. Found: C, 75.21; H, 5.20; V, 4.36; Si, 9.71.

Preparation of Tris(triphenylsilyl)vanadate(V).—Tris(triphenylsily)vanadate(V) is prepared by the reaction of triphenylsilanol and vanadium oxytrichloride in the presence of ammonia.

For a typical preparation, a solution of triphenylsilanol was prepared by dissolving 13.8 g. (0.05 mole) of triphenylsilanol in 150 ml. of anhydrous benzene. Vanadium oxytrichloride was prepared by boiling anhydrous vanadium(V) oxide with an excess of thionyl chloride until evolution of sulfur dioxide ceased. The crude vanadium oxytrichloride was distilled and 2.75 g. (0.0159 mole) of the sample boiling at 126–127° (lit., b.p. 126°) dissolved in 60 ml. of anhydrous benzene.

The solution of triphenylsilanol was put in a 500-ml. three-neck round-bottom flask fitted with a condenser protected by a barium oxide drying tube, a separatory funnel fitted with a delivery tube long enough to dip below the level of the solution, and an inlet tube for the admission of dry ammonia.[5,6] The solution of vanadium oxytrichloride in benzene was added slowly from the separatory funnel. Immediately after the first few drops of vanadium oxytrichloride solution was added, dry ammonia was allowed to bubble through the solution. A magnetic stirrer provided additional agitation. There was only a slight heat of reaction and external cooling was not necessary in order to keep the reaction vessel at room temperature.

A white flocculent precipitate of ammonium chloride, which may have been contaminated with a small amount of a purple, unidentified, ammonolysis product of vanadium oxytrichloride if vanadium oxytrichloride were in excess, was removed by filtration and the orange-yellow filtrate was concentrated by distillation at reduced pressure.

A large quantity of very pure tris(triphenylsilyl)vanadate(V) appeared by the time the solution was concentrated to 140 ml. Product contaminated with trace amounts of triphenylsilanol appeared on concentration to 70 ml. Final evaporation to dryness gave a mixture of product and unchanged triphenylsilanol. The impure material was washed thoroughly with ether and water to remove contaminating triphenylsilanol and ammonium chloride. The over-all yield was 95% based upon vanadium oxytrichloride; m.p. 225–226°. Mol. wt.: calcd., 892 g./mole; found, 886 and 860 g./mole. We have used this reaction to prepare upwards of 125 g. of pure product in one run.

Anal. Calcd. for $[(C_6H_5)_3SiO]_3VO$: C, 72.57; H, 5.04; V, 5.71; Si, 9.41. Found: C, 72.77; H, 5.21; V, 5.56; Si, 9.37.

Quite unexpectedly, it was found that tris(triphenylsilyl)vanadate(V) could also be prepared by air oxidation of a solution of vanadium(IV) chloride and sodium triphenylsilanolate. The solutions were prepared and the reaction run as described for the preparation of the vanadium(IV) product, but without the use of an inert or reducing atmosphere.

The vanadium(V) compound was recovered in 95% yield. The melting point was 225°; a mixed melting point with the tris(triphenylsilyl)vanadate(V) prepared by the previous method was 224°; the infrared spectra and X-ray powder patterns were identical.

Anal. Calcd. for $[(C_6H_5)_3SiO]_3VO$: C, 72.57; H, 5.04; Si, 9.42; V, 5.71. Found: C, 72.43; H, 4.97; Si, 9.23; and V, 5.64.

Preparation of Tris(triphenylsilyl)thiovanadate(V).—The oxidation of vanadium(IV) to vanadium(V) during the reaction of sodium triphenylsilanolate and vanadium(IV) chloride in the presence of air suggested that the new compound tris(triphenylsilyl)thiovanadate(V) might be obtained if the reaction were to be done in the presence of elemental sulfur.

A solution of 1.8 g. (0.0094 mole) of vanadium(IV) chloride in 75 ml. of anhydrous benzene was added dropwise with stirring to a slurry of 1.2 g. (0.0375 mole) of sulfur and 7.5 g. (0.0252 mole) of sodium triphenylsilanolate in 100 ml. of benzene. The solution was blanketed with dry nitrogen at all times. After the vanadium(IV) chloride solution was added, the solution was stirred vigorously for 1 hr. and allowed to stand overnight. The mixture of sodium chloride and an unidentified vanadium-containing product was removed by filtration and the filtrate evaporated to dryness *in vacuo* at room temperature. The crude product (5.5 g.) was washed thoroughly with dry diethyl ether and then recrystallized three times from warm but not boiling anhydrous diethyl ether. The pale yellow material melted sharply at 200–202°.

The compound did not decompose in cold water, but after four recrystallizations from wet acetone was found to be converted quantitatively to tris(triphenylsilyl)vanadate(V).

Anal. Calcd. for $[(C_6H_5)_3SiO]_3VS$: C, 71.3; H, 4.95; S, 3.50; Si, 9.25; and V, 5.61. Found: C, 70.4; H, 4.99; S, 3.49; Si, 9.14; and V, 5.24. Mol. wt.: calcd., 908; found, 862.

Analytical Procedures.—Usual techniques for determining vanadium and silicon in these compounds are somewhat laborious. We find the following method both convenient and accurate.

A weighed sample (0.3 to 0.4 g.) of the siloxy vanadium ester was slurried with 50 ml. of 6 *M* sodium hydroxide solution and hydrolyzed to a soluble inorganic vanadium compound and insoluble hexaphenyldisiloxane by digesting for 3 hr. at 90°. After the digestion, the solution was adjusted to about pH 9 with sulfuric acid and heated at 90° for another 10–15 min. The hot solution was filtered through a tared Gooch crucible and the crucible then dried to constant weight at 110°. The silicon was weighed as hexaphenyldisiloxane.

Best results were obtained if the sample size were chosen so as to contain between 0.03 and 0.06 g. of silicon. The conditions for hydrolysis were quite critical; excessive boiling gave low results due to decomposition of the hexaphenyldisiloxane and insufficient reaction time gave high results due to incomplete hydrolysis of the V—O—Si system.

Vanadium may be determined by analysis of the acidified filtrate from the sodium hydroxide hydrolysis.

The vanadium must be in the +5 oxidation state. In the analysis of the tetrakis(triphenylsiloxy)vanadium(IV) material, complete conversion of the vanadium(IV) to vanadium(V) was ensured by addition of a little hydrogen peroxide to the solution and boiling.

The solution containing the vanadium(V) was buffered to pH 4.5 by adding 20 ml. of 20% ammonium acetate solution and then either dilute ammonia or acetic acid. Fifteen milliliters of a 2% solution of 8-quinolinol in 5% acetic acid was then added slowly with rapid stirring. A dark green precipitate formed immediately. The slurry was heated to boiling for 5–10 min. The precipitate turned from green to black. The slurry was then filtered through a tared Gooch crucible, washed with two 10-ml. portions of 5% ammonium acetate solution, and dried to constant weight at 120°.

Gooch crucibles with medium fiber acid-washed asbestos mats of medium thickness are ideal for collecting both the hexaphenyldisiloxane and the vanadium-8-quinolinol complex. Retention is excellent and filtering is rapid. Scintered

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glass crucibles clog easily and are not too useful in these determinations.

As a check on our analytical procedures, samples of the tris-(triphenylsilyl)vanadate(V) and tetrakis(triphenylsiloxy)vanadium(IV) were analyzed by a commercial laboratory. The results were:

Sample	Calcd.	Commercial lab	This lab
$[(C_6H_5)_3SiO]_3VO$	V 5.71	5.64	5.62
	Si 9.42	9.23	9.46
$[(C_6H_5)_3SiO]_4V$	V 4.42	4.7	4.33
	Si 9.75	10.00	9.56

Synthesis of 2-Anilinoethanethiol by Hydride Reduction

C. W. SCHIMELPFENIG

Department of Chemistry, North Texas State University, Denton, Texas

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Since the discovery that several classes of compounds protected organisms from otherwise lethal doses of ionizing radiation,[1] a great deal of effort has been directed toward the synthesis of homologs of the protective compounds. Among the functional groups in protective molecules are the amino and mercapto groups. Our investigation concerning mercaptoethylation of amines has led to novel syntheses of 2-anilinoethanethiol and to an unexpected reaction of 3-phenylrhodanine.

By reducing 2-mercaptoacetanilide with lithium aluminum hydride, 2-anilinoethanethiol was prepared. By treating 2,2′′-dithiobisacetanilide in the same manner, the same aminothiol was prepared.

Incidental to this work, we had occasion to attempt the reduction of 3-phenylrhodanine with the thought that a substituted 2-aminoethanethiol might be produced in such a reaction. However, there were produced *N*-methylaniline and a number of products which could not be separated by fractional distillation. The formation of *N*-methylaniline undoubtedly involves a complete removal of sulfur from C-2 and a cleavage of the nitrogen-to-carbonyl amide bond. Examples of hydrogenolysis of sulfur during reduction by metal hydrides have been found by others,[2] as have examples of amide cleavage.[3] While there is no way of knowing which bonds are broken first, a pertinent comparison might be made with the reductive cleavage of *N*-methylanilides.[4]

Experimental

Materials.—2-Mercaptoacetic acid (trademark "Thiovanic Acid") was a gift of Evans Chemetics, Inc. Dithiodiacetic acid (dithiodiglycolic acid) was purchased from Aldrich Chemical Co. and recrystallized from ethyl acetate–benzene. 2-Mercaptoacetanilide was prepared by a modification of the method of VanAllan[5] in which water was removed with a Dean-Stark water separator instead of being removed by distillation through an esterification column.

2,2′′-Dithiobisacetanilide.—A mixture of 54.6 g. (0.3 mole) of dithiodiacetic acid, 55.8 g. (0.6 mole) of aniline, and 600 ml. of benzene was heated in a 1-l. flask equipped with a Dean-Stark water separator surmounted by a reflux condenser carrying a calcium chloride drying tube. After 4 days, 9.6 ml. of water had collected. The contents of the flask were poured into an equal volume of hexane. The resulting suspension was filtered. The precipitated 2,2′′-dithiobisacetanilide, after recrystallization from acetone, weighed 42.8 g. (43%) and had m.p. 161–163° (reported,[6] 165–166°).

2-Anilinoethanethiol.—To a dry 1-l. flask, flushed with nitrogen, carrying a calcium chloride drying tube, and equipped for stirring magnetically, were added 500 ml. of tetrahydrofuran, 19 g. (0.5 mole) of lithium aluminum hydride, and 50.2 g. (0.3 mole) of 2-mercaptoacetanilide. After stirring for 3 days at room temperature, the reaction mixture was treated with 50 ml. of water and filtered. The filtrate consisted of tetrahydrofuran and water. To a suspension of the precipitate and 1 l. of water was added 43 ml. (0.5 mole) of concentrated hydrochloric acid. This suspension was extracted with ether. After evaporation of ether from the dried extract, there was obtained 16.8 g. (37%) of 2-anilinoethanethiol, b.p. 110–112°/3 mm., n^{20}_{D} 1.6041 (reported,[7,8] b.p. 95–97°/2.5 mm., n^{20}_{D} 1.6040, n^{25}_{D} 1.6022). The product was further characterized by the *N*-acetyl derivative with m.p. 64.5–65.5° (reported,[7] 65–66°).

When 39.8 g. (0.12 mole) of 2,2′′-dithiobisacetanilide was treated with lithium aluminum hydride in the same way, 22.3 g. (61%) of 2-anilinoethanethiol was produced.

Reduction of 3-Phenylrhodanine.—In a manner similar to that described above, 20.9 g. (0.1 mole) of 3-phenylrhodanine[9] was treated with 11.4 g. (0.3 mole) of lithium aluminum hydride in tetrahydrofuran. After hydrolysis, the mixture was filtered. After removing water and tetrahydrofuran from the filtrate, there remained 4.62 g. of a yellow liquid. This liquid was distilled through a spinning band column. There was obtained 3.12 g. (30%) of *N*-methylaniline, b.p. 187–191°/752 mm., whose infrared spectrum was identical with that of authentic *N*-methylaniline and whose *p*-toluenesulfonamide was identical with the derivative prepared from the authentic amine.

After adding hydrochloric acid to the precipitate–water suspension, the mixture was extracted with ether. The extract was dried and the ether was removed by distillation. The residual red liquid, 3.2 g., distilled over the range 54–90°/10 mm. Infrared spectra of various fractions indicated the presence of amino, hydroxyl, mercapto, and monosubstituted benzene groups, but none was superimposable upon the spectrum of 2-anilinoethanethiol.

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