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Reactions of Trimethylsilyl Sulfate[1]

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The Flood Reaction.—In 1933 Flood reported that treatment of a concentrated sulfuric acid solution of hexaethyldisiloxane with ammonium chloride or fluoride gives triethylchlorosilane or the corresponding fluoro compound.[2] In connection with studies of organosilicon compounds, we have found this reaction extremely convenient for the preparation of large amounts of trialkylchloro- and trialkylfluorosilanes, when certain modifications of the procedure reported by Flood are employed.[3] During a study of the mechanism of the reaction, we isolated trimethylsilyl sulfate, a white crystalline solid, m. p. 56–58°, from the reaction of hexamethyldisiloxane with fuming sulfuric acid.[4]

In the present work it has been found that the use of concentrated sulfuric acid and continuous extraction of the reaction mixture with pentane gives improved yields and a consistently purer product.

$$[(CH_3)_3Si]_2O + H_2SO_4 \longrightarrow [(CH_3)_3Si]_2SO_4 + H_2O \quad (1)$$

To 162.0 g. (1.00 mole) of hexamethyldisiloxane was added dropwise over a two-hour period, with stirring and salt–ice cooling, 260 g. (2.5 moles) of concentrated sulfuric acid. The final reaction mixture was a white, crystalline slurry. It was continuously extracted with dry pentane for forty-eight hours while keeping the reaction mixture ice-cold. The pentane was removed from the extract under vacuum and there was obtained 161.0 g. (0.67 mole) of white crystalline trimethylsilyl sulfate. A weighed sample gave: % SO_4, 38.9 (calcd., 39.6). The acid residue remaining after extraction was hydrolyzed and there was recovered 48 g. (0.30 mole) of hexamethyldisiloxane. The yield of sulfate was 66% based on the total starting material and 94% based on unrecovered starting material.

Treatment of a heptane solution of trimethylsilyl sulfate with hydrogen chloride gas in the presence of ammonium sulfate gives an instantaneous reaction affording an 88% yield of trimethylchlorosilane.

$$[(CH_3)_3Si]_2SO_4 + 2HCl \longrightarrow 2(CH_3)_3SiCl + H_2SO_4 \quad (2)$$

Dry hydrogen chloride passed into a mixture of 20.0 g. (0.15 mole) of ammonium sulfate and 200 cc. of a *n*-heptane solution of 30.0 g. (0.124 mole) of trimethylsilyl sulfate gave immediate precipitation of droplets of sulfuric acid. After completion of the reaction (one and one-half hours), the upper layer was fractionated to give 24.0 g. (0.22 mole) of trimethylchlorosilane, b. p. 56–58°, 88% yield.

Reactions 1 and 2 suggest that the preparation of trialkylchlorosilanes by the Flood reaction involves (a) formation of the sulfate from disiloxane and sulfuric acid, and (b) reaction of the sulfate with hydrogen chloride to give the chlorosilane.

$$(R_3Si)_2O + H_2SO_4 \longrightarrow (R_3Si)_2SO_4 + H_2O \quad (a)$$

$$(R_3Si)_2SO_4 + 2HCl \longrightarrow 2R_3SiCl + H_2SO_4 \quad (b)$$

Both of these reactions are reversible. Hydrolysis of trimethylsilyl sulfate with water readily gives the disiloxane. An effective reversal of (b) has been utilized by Patnode and Schmidt[5] in the preparation of trimethylsilyl sulfate from trimethylchlorosilane and concentrated sulfuric acid.

In the Flood reaction, isolation of trimethylchlorosilane in good yield is made possible by the presence of ammonium bisulfate, from the reaction of ammonium chloride with sulfuric acid, which effectively prevents the reversal of (b).

Addition of 108 g. (1.0 mole) of trimethylchlorosilane to a mixture of 245 g. (2.5 moles) of concentrated sulfuric acid and 99 g. (0.75 mole) of ammonium sulfate, followed by stirring for fifteen minutes gave a very slight evolution of hydrogen chloride. Separation of the upper layer,

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(1) Presented at the 110th Meeting of the American Chemical Society, Chicago, Ill., September 1946. Paper XIV in a series on organosilicon compounds. For paper XIII see THIS JOURNAL, **70**, 435 (1948).

(2) Flood, *ibid.*, **55**, 1735 (1933).

(3) See Di Giorgio, Strong, Sommer and Whitmore, *ibid.*, **68**, 1380 (1946); Sommer, Bailey, Strong and Whitmore, *ibid.*, **68**, 1881 (1946); Pray, Sommer, Goldberg, Kerr, Di Giorgio and Whitmore, *ibid.*, **70**, 433, (1948).

(4) Sommer, Pietrusza, Kerr and Whitmore, *ibid.*, **68**, 156 (1946).

(5) Patnode and Schmidt, *ibid.*, **67**, 2272 (1945).

followed by fractionation, gave 94.6 g. (0.87 mole) of trimethylchlorosilane, a recovery of 87%.

Although hydrogen chloride gave no apparent reaction with a solution prepared from hexamethyldisiloxane and concentrated sulfuric acid in the absence of added ammonium sulfate, the following procedure gave a 65% yield of trimethylchlorosilane. Dry hydrogen chloride was passed into a stirred solution (at 0°) prepared from 162 g. (1.0 mole) of hexamethyldisiloxane and 250 g. (2.5 moles) of concentrated sulfuric acid, while adding ammonium sulfate intermittently to the reaction mixture over a three-hour period until a total of 200 g. (1.5 moles) had been added. Hydrogen chloride was then passed in for an additional two hours, until fumes of hydrogen chloride were evolved from the condenser. The upper layer was separated and fractionated, yielding 141 g. (1.13 moles) of trimethylchlorosilane, 60% yield. On cooling, the residue from the fractionation gave 68.0 g. (0.25 mole) of trimethylsilyl sulfate crystals. Thus 90% of the hexamethyldisiloxane was accounted for.

It has recently been reported that hydrogen chloride and hexamethyldisiloxane react to give trimethylchlorosilane.[6] Thus it is possible that the following reaction of hexamethyldisiloxane, or an oxonium salt thereof, should be added to reactions (a) and (b) above in order to fully represent the Flood reaction.

$$(\mathrm{R_3Si})_2\mathrm{O} + 2\mathrm{HCl} \longrightarrow 2\mathrm{R_3SiCl} + \mathrm{H_2O} \qquad \text{(c)}$$

Reaction (c), like (a) and (b), is reversible.

Other Reactions of Trimethylsilyl Sulfate.—Like trimethylchlorosilane,[7] trimethylsilyl sulfate reacts with ammonia gas to give hexamethyldisilazane, and with dilute alkali to give azeotropic hexamethyldisiloxane–trimethylsilanol and hexamethyldisiloxane.

$$[(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{SO_4} \xrightarrow{\mathrm{NH_3}} [(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{NH}$$

$$[(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{SO_4} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaOH}} [(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{O} + (\mathrm{CH_3})_3\mathrm{SiOH}$$

Treatment of 300 cc. of an ether solution of 35.0 g. (0.145 mole) of trimethylsilyl sulfate with dry ammonia gas gave immediate reaction. When ammonia was no longer absorbed (three hours), filtration of the product to remove the precipitated ammonia salt followed by fractional distillation gave 16.5 g. (0.102 mole) of hexamethyldisilazane, b. p. 124°, n^{20}_{D} 1.4077, 71% yield.

Trimethylsilyl sulfate, 60 g. (0.25 mole), dissolved in 150 cc. of dry ether, was added (two hours) with vigorous stirring to 200 cc. of ice-cold 20% aqueous sodium hydroxide by means of a separatory funnel having a capillary stem extending below the surface of the alkali. The ether layer was separated, the aqueous layer extracted with three 100-cc. portions of ether, and the ether solution of the product dried with potassium carbonate. Fractionation gave 14.7 g. of azeotropic hexamethyldisiloxane–trimethylsilanol, b. p. 90–93°, n^{20}_{D} 1.3778–1.3790, and 13.3 g. of hexamethyldisiloxane, b. p. 97–100°, n^{20}_{D}1.3774.

Trimethylsilyl sulfate gave the tetraalkylsilane in good yield when treated with ethyl- or *n*-propylmagnesium bromide. Isopropylmagnesium bromide gave mainly trimethylbromosilane in one experiment, and a 34% yield of isopropyltrimethylsilane in another experiment when a longer reaction time was used.

Ethylmagnesium Bromide.—A solution of 30.0 g. (0.33 mole) of trimethylsilyl sulfate in 200 cc. of dry ether was added, with stirring, to 0.9 mole of ethylmagnesium bromide in 250 cc. of ether during ten minutes. There was no vigorous reaction at first, but addition of about two-thirds of the sulfate resulted in the formation of two layers. The reaction mixture was then slowly heated on the steam-bath until all of the volatile material was distilled and collected. After heating for six hours, the solid in the flask appeared to be dry, and was allowed to cool. Hydrolysis with dilute acid and extraction gave no additional product. After removal of ether, the distillate from the reaction mixture was fractionally distilled. There was obtained 36.0 g. (0.55 mole) of ethyltrimethylsilane,[8] b. p. 62°, n^{20}_{D} 1.3820, a yield of 83.5%.

***n*-Propylmagnesium Bromide.**—Using a procedure similar to that above, 0.8 mole of *n*-propylmagnesium bromide was treated with 73 g. (0.3 mole) of trimethylsilyl sulfate. Fractional distillation indicated that the product was a mixture of *n*-propyltrimethylsilane and trimethylbromosilane.[9] Since these compounds were somewhat difficult to separate, the trimethylbromosilane (*ca.* 10%) was removed by hydrolysis followed by treatment with concentrated sulfuric acid which dissolved the formed hexamethyldisiloxane and left *n*-propyltrimethylsilane as a clear upper layer. The yield of *n*-propyltrimethylsilane,[8] b. p. 90°, n^{20}_{D} 1.3929, was 55%.

Isopropylmagnesium Bromide. Run 1.—A solution of 73 g. (0.30 mole) of trimethylsilyl sulfate in 150 cc. of dry ether was added to 0.7 mole of isopropylmagnesium bromide in 350 cc. of ether. The reaction mixture was stirred at room temperature for one hour and was then heated on the steam-bath for six hours to distil all of the volatile product. The distillate fumed vigorously on exposure to air. Fractionation gave 47.5 g. (0.31 mole) of trimethylbromosilane,[9] b. p. 80°, a yield of 51.5%.

Run 2.—A run similar to that above was made, except that the reaction mixture was stirred at reflux temperature for eight days before distillation of the product. Fractionation gave 15.7 g. (0.155 mole) of isopropyltrimethylsilane, b. p. 89°, n^{20}_{D} 1.3958, a yield of 34%.

Anal. Calcd. for $\mathrm{C_6H_{16}Si}$: Si, 24.1. Found: Si, 23.9.

The physical properties of this material check those of another sample prepared from *i*-propyltrichlorosilane[10] and methylmagnesium bromide.

Heating of trimethylsilyl sulfate with dry ammonium chloride gave trimethylchlorosilane in fair yield.

$$[(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{SO_4} \xrightarrow{\mathrm{NH_4Cl}} 2(\mathrm{CH_3})_3\mathrm{SiCl}$$

In a 250-cc. distilling flask were placed 40.0 g. (0.166 mole) of trimethylsilyl sulfate and 16.0 g. (0.33 mole) of dry powdered ammonium chloride. The flask was fitted with a thermometer, whose bulb was just below the side-arm, and a water-cooled condenser attached to an adaptor. The reaction mixture was heated gently and almost immediately vapor entered the condenser. The reaction mixture was heated until it was dry, and the distillate was fractionally distilled. There was obtained 15.0 g. (0.138 mole) of trimethylchlorosilane,[11] b. p. 56–58°, 32.5% Cl (calcd. 32.6% Cl), 42% yield.

Using a procedure similar to that above, very poor yields of trimethylchlorosilane (5–10%) were obtained with cupric chloride and cuprous chloride.

It is of interest to note that one of the most striking differences between trimethylsilyl sulfate and alkyl sulfates is the tendency of the latter to give reaction of only one of the alkyl groups.[12]

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(6) Krieble and Elliott, THIS JOURNAL, **68**, 2291 (1946).

(7) Sauer, *ibid.*, **66**, 1707 (1944).

(8) Whitmore, Sommer, Di Giorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, *ibid.*, **68**, 475 (1946).

(9) Gilliam, Meals and Sauer, *ibid.*, **68**, 1161 (1946).

(10) Booth and Spessard, *ibid.*, **68**, 2660 (1946).

(11) Taylor and Walden, *ibid.*, **66**, 842 (1944); Gilliam and Sauer, *ibid.*, **66**, 1793 (1944).

(12) Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 48.

This is in line with the increase in reactivity of electronegative groups which generally results from substitution of silicon for carbon.

Summary

1. Trimethylsilyl sulfate has been prepared by an improved method.

2. Reactions of trimethylsilyl sulfate have been studied.

3. A mechanism for the Flood reaction has been proposed.

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[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Isolation of β-Amyrin and a Fatty Acid of High Molecular Weight from *Solidago leavenworthii* T. and G.

BY R. C. BURRELL AND FORREST G. HOUSTON

In the usual process for obtaining rubber from goldenrod the leaf material is first exhaustively extracted with acetone to remove waxes and resinous materials. On evaporation of the acetone from this extract a dark green tar is obtained. Polhamus[1] reports a mean of 21.03% of tar from five samples of *Solidago minor*. At the Southern Regional Research Laboratory of the U. S. D. A., Guthrie, *et al.*,[2] obtained a good yield of quercitrin and its aglycone from such tar prepared from the leaves of *Solidago leavenworthii* T. and G. Through the kindness of Dr. Guthrie a sample of this tar was obtained by us and the benzene soluble fraction of it was subjected to further investigation.

Experimental Results

Isolation of β-Amyrin.—Three kg. of the above mentioned tar were extracted with 2 l. of boiling benzene followed by five extractions with one-liter portions of hot benzene. The combined extracts were filtered through paper pulp and the green pigments removed by treatment with activated charcoal. A dark brown solution resulted from which the benzene was distilled, thereby yielding 950 g. of a brown viscous oil. This oil was refluxed for two hours with 1500 cc. of 20% alcoholic potassium hydroxide. The mixture was cooled and 2 liters of water added. It was made slightly acid to litmus with 10 *N* sulfuric acid. Two layers were formed, the upper a brown oil and the lower a greenish colored water solution. The oily layer was separated and treated with one liter of 10% sodium hydroxide solution and 3 liters of water and shaken vigorously for an hour. This mixture was then repeatedly extracted with ether, the extracts united, washed and dried over anhydrous sodium sulfate.

The sodium hydroxide solution which remained after the ether extraction was set aside for further investigation.

The ether was distilled from the dried extract leaving a deep yellow greasy residue. This was dissolved in one liter of acetic anhydride and refluxed for two hours. After standing overnight a heavy deposit of yellow needles formed. The liquid was then decanted and the crystals washed twice with one-liter portions of hot 95% ethyl alcohol and finally with petroleum ether until colorless. Nineteen grams of vacuum dried crystals was obtained, amounting to a yield of about 0.13% of the dried leaf material.

These crystals (acetate) melted at 231–233°. The saponification equivalent was 467 to 471 and the specific rotation in chloroform was $[\alpha]^{28}\text{D}$ +78°. The saponified compound after recrystallization from a large volume of 95% ethyl alcohol gave long colorless needles which melted at 190–192°. The benzoate melted at 229–230°. The Liebermann–Burchard reaction was positive. These properties correspond quite closely to those recorded for β-amyrin.[3,4]

Isolation of a High Molecular Weight Fatty Acid.—The fraction of saponified oil that was soluble in 10% sodium hydroxide (see β-amyrin preparation above) was neutralized with 10 *N* sulfuric acid. A brown oily liquid rose to the surface. This oil was removed by extraction with ether, the ether extract was thoroughly washed with water and dried, the ether removed by distillation and the residue dissolved in 1500 cc. of hot 95% ethyl alcohol. This solution was partially cleared with activated charcoal. On cooling a slightly yellow flocculent precipitate formed. This was reprecipitated four times from 95% alcohol.' The 5 g. of colorless, amorphous material thus obtained was saponified for six hours with 20% alcoholic potassium hydroxide. This solution was then cooled and diluted with an equal volume of water. A slightly yellowish soapy precipitate formed which was filtered off, washed with dilute sulfuric acid, dried over a steam-bath and dissolved in 30 cc. of hot glacial acetic acid. On slow cooling colorless rosets of crystals were deposited (dry wt. 1 g.) which melted at 82°. The molecular weight by the Rast method was 433. Due to the hydrocarbon-like properties of the compound neutralization equivalent values were erratic. The acid amide melted at 108–110°.

Anal. Calcd. for $C_{28}H_{56}O_2$ (424.4): C, 79.17; H, 13.29. Found: C, 79.27; H, 13.25.

Summary

The isolation of β-amyrin and a high molecular weight fatty acid from the acetone extract of leaves of *Solidago leavenworthii* T. and G. is described.

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(1) L. G. Polhamus, *J. Agr. Research*, **47**, 149 (1933).

(2) J. D. Guthrie, R. T. O'Connor, M. F. Stansbury and T. R. Savich, THIS JOURNAL, **66**, 1794–1795 (1944).

(3) Abderhalden, "Biochemisches Handlexikon VII," 729 (1912).

(4) I. M. Heilbron, G. L. Moffet and F. S. Spring, *J. Chem. Soc.*, 1583 (1934).