butoxy-diaminosilane. The presumed di-*t*-butyl-di-(2-ethylaminoethyl) silicate boiled at 285° at 740 mm. and did not decompose appreciably upon being refluxed at this temperature for one hour. Variation of conditions by adding the diaminosilane to the refluxing amino alcohol and *vice versa* appeared to give no improvement in eliminating or minimizing the formation of the side-product arising presumably by ester-interchange.

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THE WHITMORE LABORATORY
SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Solubility and Specific Rotation of *l*-Ascorbyl Palmitate and *l*-Ascorbyl Laurate

BY DANIEL SWERN

Renewed interest in *l*-ascorbyl palmitate,[2] resulting from its recently reported antiscorbutic activity,[3] non-toxicity[4] and commercial availability[5] has prompted us to determine its solubility at 25° in some typical organic solvents, water, and cottonseed and peanut oils. For purposes of comparison, we also determined the solubility of *l*-ascorbyl laurate[2] in the two vegetable oils. We have also determined the specific rotation of both *l*-ascorbyl palmitate and laurate. With the exception of water and petroleum naphtha, the temperature coefficient of solubility is high. Benzene and ethyl acetate are two of the best crystallizing solvents for purifying the esters.

Experimental

Solubility Determinations.[6]—Solubility in petroleum naphtha, boiling range 63–70°, and water was determined on saturated solutions obtained by shaking the solvent with excess solute until equilibrium, ascertained by analysis, was attained. With all the other solvents, equilibrium was approached from the solution side by allowing excess solute to crystallize. Dissolved ester was determined either by titration with 0.1 *N* sodium hydroxide[2] or by evaporation of solvent. At least two determinations were run; precision of duplicates was about five parts per thousand. Solubility of *l*-ascorbyl palmitate in glycerol could not be determined because the solution was a thick gel. Its solubility, however, appeared to be low. Results are summarized in Table I.

Specific Rotation.—Specific rotation was determined with a Bellingham and Stanley Glass Scale polarimeter that could be read directly to 0.01°. A 5–10% solution of the ester in 95% alcohol and a 4.00-dm. tube were employed.

TABLE I

SOLUBILITY AT 25 ± 0.10°: *l*-ASCORBYL ESTERS

Solvent	Sol.[a] g./100 g.	Solvent	Sol.[a] g./100 g.
Palmitate		Palmitate	
Water[b]	0.56	Ethyl acetate	4.9
Petroleum naphtha[c]	0.00	Ethyl cellosolve[e]	>33.9
Ethanol 95%[d]	23.5	Peanut oil	0.18
Benzene	0.45	Cottonseed oil	0.22
Ethylene glycol	0.18	Laurate	
1,2-Propylene glycol	6.6	Peanut oil	0.11
Dioxane	19.0	Cottonseed oil	0.08

[a] By titration. [b] Solubility by evaporation 0.31 g./100 g. Small and probably variable quantities of solute emulsified, thus accounting for the poor duplication between the results by titration and by evaporation. [c] B. p. range 63–70°. Solubility by evaporation 0.01 g./100. [d] Solubility by evaporation 23.4 g./100. [e] Insufficient material to complete determination.

l-Ascorbyl palmitate: $[\alpha]^{25.5}\text{D}$ + 23.3° (8.086 g. per 100 ml. of 95% ethanol solution). *l*-Ascorbyl laurate: $[\alpha]^{25.5}\text{D}$ + 26.6° (5.014 g. per 100 ml. of 95% ethanol solution).

PHILADELPHIA 18, PENNA. RECEIVED JANUARY 26, 1949

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Swern, Stirton, Turer and Wells, *Oil and Soap*, **20**, 224 (1943).

(3) Ambrose and DeEds, *Arch. Biochem.*, **12**, 375 (1947).

(4) Fitzhugh and Nelson, *Proc. Soc. Exptl. Biol. Med.*, **61**, 195 (1946).

(5) Chas. Pfizer and Company, New York, N. Y.

(6) Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, pp. 111 and 341.

Preparation of Fluorothiophene

BY ROBERT T. VANVLECK

Chloro- and bromothiophene are offered in the industrial market and iodothiophene is reported in the literature, but no reference has been made to fluorothiophene. This compound has been prepared in these Laboratories in small yields by the reaction of antimony trifluoride with iodothiophene in the presence of nitromethane as a solvent. The preparation of fluorothiophene from 2-iodothiophene indicates that the fluoro compound is the 2-isomer.

Nitroethane, nitropropane and *t*-butylthiophene were found not suitable as solvents for the reaction. Various other methods for preparing fluorothiophene proved unsuccessful; they include the reaction of antimony trifluoride with either chloro- or bromothiophene, the reaction of aluminum trifluoride with chlorothiophene, and the reaction of fluoboric acid with thiophene diazonium chloride. This last reaction was studied in an unsuccessful attempt to adapt Flood's synthesis of fluorobenzene[1] to the preparation of the thiophene analog. It is possible that the diazonium chloride was not obtained due to the instability of the aminothiophene.

Experimental

A mixture of 150 g. (0.72 mol) of iodothiophene and 43 g. (0.24 mole) of antimony trifluoride in 250 ml. of nitromethane was heated in a flask at reflux temperature (90–100°) for five hours; the product fluorothiophene distilled over through a small column as formed plus some

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(1) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 295.

solvent. The distillate was washed with thiosulfate solution to remove a small amount of free iodine, the organic layer separated and dried over calcium chloride. Distillation produced about a ten mole per cent. yield of the new compound, fluorothiophene, a water white liquid, boiling at 82° and having a refractive index of 1.4971, 20°/D.

Anal. Calcd. for C_4H_3SF: S, 31.37; F, 18.6. Found: S, 31.45; F, 18.0.

BEACON LABORATORIES
THE TEXAS COMPANY
BEACON, NEW YORK

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Extraction of Cerium(IV) Nitrate by Butyl Phosphate[1a]

BY JAMES C. WARF[1b]

The extraction of inorganic compounds by organic solvents sometimes affords a unique method for rapidly and easily separating compounds of certain metals from common impurities. Well-known examples include the characteristic extraction of iron(III) chloride and the chlorides of a few other metals by ether, the extraction of uranyl nitrate by ether, the extraction of silver perchlorate by toluene,[2] and more recently the extraction of thorium nitrate by methyl isobutyl ketone and other solvents.[3] The extraction of cerium(IV) nitrate by ether was employed by Imre,[4] who observed that the solvent was attacked, generating heat and necessitating cooling, and that high nitric acid concentrations were required for efficient extraction. Pure ceria, however, could be produced.

A number of solvents expected to be resistant to the strong oxidizing action of cerium(IV) nitrate were tested, and nitromethane and tri-*n*-butyl phosphate found to be most satisfactory. The extent of removal of the cerium from the aqueous phase was also investigated.

Ammonium hexanitratocerate(IV) from the G. Frederick Smith Chemical Co. was employed. Tri-*n*-butyl phosphate from the Eastman Kodak Co. was vacuum distilled, the portion boiling at 145–150° (8 mm.) being collected separately; it was saturated with water before use.

The degree of stability of the solvent toward oxidation by the solute was established by permitting portions of solutions 0.5 *F* in ammonium hexanitratocerate(IV) and 1.0 *F* in nitric acid to stand at room temperature with the solvent for increasing periods of time, after which the cerium(IV) content was determined by titration with iron(II) sulfate solution using tris-(1,10-phenanthroline)-iron(II) sulfate as indicator.

The extent of extraction of the cerium(IV) nitrate was determined similarly by separating layers and titrating each immediately. The solvent layer was scrubbed several times with a solution 1.0 *F* each in nitric acid and ammonium nitrate before re-extraction of the cerium.

The rate of reduction of the cerium(IV) nitrate by butyl phosphate under the conditions described is indicated by the following results: After 1.6 hours, 1% of the total cerium(IV) was reduced; after 35 hours, 5%; after 120 hours, 10%; after 500 hours, 31%; and after 820 hours, 45%.

Conditions for favorable extraction were found to cover a wide range, 98–99% of the cerium entering the solvent when equal phase volumes were employed, regardless of the ammonium nitrate and nitric acid concentrations. The presence of nitric acid was found necessary to promote clean separation of the layers. At extreme dilution (0.001 *F* Ce(IV)) less favorable partition was observed, only 60–70% being extracted. Solutions of ammonium hexanitratocerate(IV) in 1.0 *F* nitric acid were used most frequently. Aqueous phases after extraction were colorless, and a few per cent. of the cerium(IV) was reduced to cerium(III) during the course of the operations. Addition of ammonium acetate or perchlorate to the aqueous phase had little effect on the degree of extraction, but ammonium sulfate caused serious interference.

Recovery of the cerium from the butyl phosphate by re-extraction with water or dilute nitric acid was slow and laborious, although the use of ammonium sulfate solutions was feasible. Generally the cerium(IV) was quickly and quantitatively re-extracted through reduction to cerium(III) by hydrogen peroxide; hydroxylamine, formaldehyde or glucose also were employed. Evaporation of aqueous solutions of the recovered cerium(III) salts and ignition yielded gray or black products, owing to the presence of pyrophosphates. This difficulty was avoided by washing the water phase thoroughly with benzene or carbon tetrachloride, to remove the small quantity of dissolved butyl phosphate, before evaporation or precipitation of cerium(III) oxalate. Cerium(IV) oxide resulting on ignition after such treatment was practically pure white, and contained negligible amounts of phosphorus.

Over 99.5% of the cerium could be removed from cerium(III) nitrate solutions by first oxidizing electrolytically as recommended by Smith, Frank and Kott,[5] in three steps, each followed by a butyl phosphate extraction. It was found more convenient to perform the oxidation chemically, using bromates in strong nitric acid solution, a procedure first employed by Schuman.[6] In order to realize quantitative removal of the cerium, a small continuous extractor was used.

A U-tube stirrer-extractor, described by Huzise,[7] was constructed. It was charged with 100–150 ml. of a solution 0.2 *F* in cerium(III) nitrate, 8–10 *F* in nitric acid, and 3 *F* in sodium nitrate. Small portions of solid sodium bromate were added over a period of two to three hours, using a total of 3 g., while butyl phosphate was run

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[1a] Based on work done for the Manhattan District (Contract No. W-7405 eng-82), F. H. Spedding, Project Director. First recorded in Plutonium Project reports CC-2402 (April 3, 1945) and ISC-8 (August 7, 1947), by J. Warf.

[1b] Present address: Department of Chemistry, University of Southern California, Los Angeles 7, California.

[2] Hill and Miller, THIS JOURNAL, **47**, 2702 (1925).

[3] Rothschild, Templeton and Hall, *J. Phys. Colloid Chem.*, **52**, 1006 (1948).

[4] Imre, *Z. anorg. allgem. Chem.*, **164**, 214 (1927).

[5] Smith, Frank and Kott, *Ind. Eng. Chem., Anal. Ed.*, **12**, 268 (1940).

[6] Schuman, Plutonium Project Report CC-2739 (February 23, 1945).

[7] Huzise, *J. Chem. Soc. Japan*, **62**, 360 (1941).