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.

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

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

[4] Inre, *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).

through the extractor, a total of 300 ml. being employed. The solvent was well dispersed by the stirrer, and rose to form a static layer in the exit arm of the U-tube, from which it drained at the same rate at which fresh solvent was added. Qualitative tests showed no detectable cerium remaining in the water phase. The butyl phosphate extracted bromine as well as cerium.

Uranyl and thorium nitrates were observed to be readily extracted by butyl phosphate. These elements can be separated by extraction of cerium(III) solutions. The extraction of iron, zirconyl and lanthanum nitrates by butyl phosphate was also studied. The results showed that excellent separation from iron, fair separation from zirconium, and rather poor separation from lanthanum can be expected.

Iron(II) nitrate solutions, containing 1 mg. to 5 g. of iron per 100 ml., and 1.0 *F* in nitric acid, were extracted with butyl phosphate, the organic layer washed with ammonium nitrate–nitric acid solution, and re-extracted with hydrogen peroxide. The amount of iron thus recovered was determined spectrophotometrically with 1,10-phenanthroline and the ratio of the amount of iron in the original aqueous phase to the amount from the organic phase taken as a "separation factor." This factor varied from 2000 for low iron concentrations to 1.6 × 10^6 for the high concentrations. Similar experiments with zirconium, using a radioactive isotope (Zr^{95}, half-life 65 days) showed separation factors of 200 to 600, while with lanthanum (La^{140}, half-life 40 hours), factors of only 80 to 100 were observed. Lanthanum nitrate solution (500 mg. of La per 100 ml.) was extracted exhaustively by the stirrer U-tube technique described above, using sodium bromate, when 4 to 7% was found to be carried over.[8]

The high degree of extraction by butyl phosphate over a wide range of conditions suggested formation of a compound between the solvent and cerium(IV) nitrate.

Absorption spectra of aqueous and butyl phosphate solutions each 0.05 *F* in cerium(IV) nitrate were identical except for a slight shift toward the longer wave lengths for the non-aqueous solution. The absorption curves had no maxima, and both solutions were transparent for wave lengths above 580 mμ. The solvents were non-absorbing for wave lengths above 400 mμ. Kjeldahl analyses of the organic phase showed that no ammonium compound was present. Treatment of small known quantities of the solvent with a large excess of cerium(IV) nitrate solution, followed by extraction with carbon tetrachloride and determination of the Ce(IV) content, showed Bu_3PO_4/Ce ratios of 2.5 ± 0.1. Butyl phosphate extracts of ammonium hexanitratocerate(IV) from solutions containing no additional nitric acid were analyzed for nitrate by the nitron method,[9] and for cerium(IV), which gave NO_3/Ce ratios of 3.3 ± 0.2. While these values do not coincide with the ratios demanded by a simple formula, there was also no assurance of complete conversion of the reactants into a single compound. The analytical work was not pursued sufficiently to establish unambiguously the identity of the extracted substance or substances.

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IOWA STATE COLLEGE
AMES, IOWA

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[8] Electrolytic oxidation is preferred to the use of bromates, for the latter seemed to permit greater extraction of iron, zirconium, and lanthanum. This may be attributable to the formation of bromides. It was observed that the behavior of zirconyl halides toward butyl phosphate extraction was quite different from that of the nitrate.

[9] Busch, *Ber.*, **38**, 861 (1905); Gutbier, *Z. angew. Chem.*, **18**, 494 (1905).

NEW COMPOUNDS

The Diacetate of 2-Methyl-1,3-pentanediol

Investigations in this Laboratory led to the preparation of the diacetate of 2-methyl-1,3-pentanediol. This new compound is of interest as it was reported by previous investigators[1] that the reaction of 2-methyl-1,3-pentanediol with acetic anhydride yields only the monoacetyl derivative.

Procedure.—One-half mole of 2-methyl-1,3-pentanediol and one-half mole of acetic anhydride were refluxed with a trace of sulfuric acid for three hours. At the end of this period, toluene was added to the reaction flask and a water-trap placed in the reflux system. The water from the reaction was then removed by refluxing with the toluene. The glycol diacetate was recovered in good yield after removal of the toluene and subsequent fractionation through a five-bulb Snyder column.

The physical constants of the diacetate of 2-methyl-1,3-pentanediol are: b. p., 225° (uncor.); d^{20}_4 1.0025; n^{20}D 1.4253; *anal.* 99% ester content as the diacetate of 2-methyl-1,3-pentanediol; mol. ref. 51.68 found; 51.56 calcd.

PETROLEUM RESEARCH AND DEVELOPMENT LABORATORY
CELANESE CORPORATION OF AMERICA
CLARKWOOD, TEXAS GUILES FLOWER, JR.[2]

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[1] Kling and Roy, *Bull. soc. chim.*, [4] **1**, 698 (1907); Kling and Roy, *Compt. rend.*, **144**, 1112 (1907).

[2] Present address: Dictaphone Corporation, Bridgeport 5, Connecticut.

Esters of 5-Methyl-2-thenoic Acid

The esters of 5-methyl-2-thenoic acid listed in Table I were prepared by refluxing 10 g. (0.07 mole) of the acid[1] in an excess (125 ml.) of the required alcohol containing 6–7 ml. of concd. sulfuric acid. After refluxing for four hours, the esters were worked up in the usual manner, and vacuum-distilled.

TABLE I

ESTERS OF 5-METHYL-2-THENOIC ACID

Ester	B. p., °C. (5 mm.)	d^{20}_4	n^{20}D	Yield, %	Sulfur, %[b] Calcd.	Found
Methyl	77–79[a]	1.1736	1.5380	71	20.53	20.70
Ethyl	87–89	1.1234	1.5233	82	18.83	18.99
n-Propyl	95–98	1.0936	1.5075	80	17.40	17.47
i-Propyl	87–88	1.0766	1.5092	44	17.40	17.14
n-Butyl	106.5–108.5	1.0668	1.4955	88	16.17	16.18
i-Butyl	102–105	1.0610	1.5082	76	16.17	16.33
n-Amyl	116–118	1.0456	1.5054	64	15.10	15.29

[a] Rinkes reported a b. p. 102° (16 mm.) (*Rec. trav. chim.*, **52**, 538 (1933)). [b] Analyses by Mrs. Betty Jarvis.

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[1] Prepared by the method of Hartough and Conley, THIS JOURNAL, **69**, 3096 (1947), in an average of 69%.

INDIANA UNIVERSITY HERSCHEL G. GROSE
BLOOMINGTON, INDIANA E. E. CAMPAIGNE

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3-(4- and 5-Methyl-2-pyridylamino)-acrylic Acids[1]

These two new derivatives of acrylic acid were prepared for biological testing at the request of the Chemical-Bio-

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[1] This work was carried out under a Grant-in-Aid from the Research Corporation.