225° (dec.); $[\alpha]^{25}\text{D}$ −16.8° (*c*, 0.48 in ethanol–chloroform 1:1); −69° (*c*, 0.22 in pyridine); ϵ at 232 mμ 52,000; 3(β)-cholestanyl benzoate, ϵ at 232 mμ 12,000.

Anal. Calcd. for $C_{27}H_{38}O_8N(C_7H_5O)_5$: C, 72.31; H, 6.17; for $C_{27}H_{39}O_8N(C_7H_5O)_4$: C, 71.32; H, 6.42. Found: C, 71.28, 71.46; H, 6.41, 6.49.

Germine Tetrapropionate.—A solution of germine (250 mg., 0.5 millimole) in pyridine (4 cc.) was mixed at 0° with freshly distilled propionic anhydride (7.6 cc., 6.0 millimoles). After standing at room temperature for 19 hours, the solvents were removed *in vacuo*. The residue crystallized in part from dilute ethanol. After two recrystallizations from the same solvent needles (10.8 mg.) melting at 216–217° were obtained, $[\alpha]^{25}\text{D}$ −92.4° (*c*, 0.24 in pyridine).

Anal. Calcd. for $C_{27}H_{39}O_8N(C_2H_5CO)_4$: C, 63.83; H, 8.10; $4C_2H_5CO$, 31.1. Found: C, 63.72; H, 8.31; C_2H_5CO, 31.0.[4]

Germine Triisobutyrate.—A solution of germine (923 mg., 1.81 millimoles) in dry pyridine (16 cc.) was mixed at −20° with freshly distilled isobutyryl chloride (1.58 g., 15.5 millimoles) in pyridine (8 cc.). The mixture was kept at −20° for a half-hour and then at 0° overnight. It was poured onto chopped ice and saturated sodium bicarbonate solution and, after some standing, exhaustively extracted with a total of 500 cc. of chloroform. The residue of the dried and evaporated extract was triturated with benzene, and the insoluble portion was removed by centrifugation. The residue obtained from the supernatant was throughly dried (970 mg.) and adsorbed in benzene solution on 20 g. of sulfuric acid-washed alumina.[1] Continued washing with benzene brought through only traces of material, but with benzene containing 2.5% methanol a substantial fraction (339 mg.) was eluted. This material was crystallized by dissolving it in the minimum amount of boiling hexane and allowing the solution to stand at 4° overnight (128 mg., m.p. 196–200°). The melting point remained virtually unchanged on 2 recrystallizations from the same solvent (197–201°); ($[\alpha]^{25}\text{D}$ −65.8 (*c*, 0.76 in pyridine).

Anal. Calcd. for $C_{27}H_{39}O_8N(C_4H_7O)_4$: C, 65.36; H, 8.55; $4(CH_3)_2CHCO$, 36.0; for $C_{27}H_{40}O_8N(C_4H_7O)_3$: C, 65.07; H, 8.54; $3(CH_3)_2CHCO$, 29.6. Found: C, 65.24, 65.02; H, 8.61, 8.63; $(CH_3)_2CHCO$[4], 31.6, 29.3.

Further elution with more polar solvent mixtures yielded only small additional amounts of material which failed to crystallize either as such or after reacylation under the above conditions.

Germine Pentacyclohexanecarboxylate.—A solution of germine (250 mg., 0.5 millimole) in dry pyridine (4 cc.) was cooled to −20° and a solution of 0.7 cc. cyclohexanecarboxylic acid chloride (770 mg., 5.25 millimoles, freshly prepared from the acid with thionyl chloride and distilled *in vacuo*) in dry pyridine (4 cc.) was added. The reaction mixture was kept at −20° for two hours, and then overnight at 4°. Treatment with ice-cold bicarbonate solution yielded a precipitate (600 mg.), which was extracted with boiling acetone. After removal of undissolved material by centrifugation the solution was concentrated to a small volume. The crystalline product which deposited on standing yielded on 2 recrystallizations from acetone prisms (21 mg.) melting at 202–205°; $[\alpha]^{25}\text{D}$ −60.4° (*c*, 0.5 in pyridine).

Anal. Calcd. for $C_{27}H_{38}O_8N(C_6H_{11}CO)_5$: C, 70.26; H, 8.84. Found: C, 70.56; H, 9.19.

The non-crystallizable esters mentioned in the general part were prepared from germine and the appropriate acyl chlorides under conditions similar to those specified for the isobutyrate. The crude products were chromatographed as described in that section. Attempts to crystallize the early benzene–2.5% methanol eluates (which were assumed to contain the most highly esterified products) were uniformly unsuccessful.

Acknowledgments.—The author is indebted to Drs. O. Wintersteiner and Josef Fried for many helpful suggestions, to Mr. Norman Salzman for able technical assistance and to Mr. Joseph F. Alicino and his associates for the microanalyses. The assays for hypotensive activity were performed by Mr. Irving Miller, Division of Pharmacology, Squibb Institute.

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RECEIVED JULY 17, 1950

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[4] Pregl-Roth, "Die quantitative organische Microanalyse," Julius Springer, Berlin, 1935, p. 235.

The Preparation and Some Properties of Curium Metal

BY J. C. WALLMANN, W. W. T. CRANE AND B. B. CUNNINGHAM

Curium metal has been prepared on the microgram scale by reduction of curium trifluoride with barium metal vapor at 1275°, using a vacuum furnace and double crucible system similar to that described by Fried and Davidson.[1]

Six successful reductions, which yielded bright metallic globules of metal ranging in mass from about 0.01 to 4 μg. have been made. The metal is silvery in appearance and about as malleable as plutonium prepared under the same conditions. The metal retained its bright appearance in the dry atmosphere of a nitrogen "dry box" for some hours but gradually tarnished, and on standing for about 24 hours was rather badly corroded. Under the same conditions, samples of other actinide metals, such as americium or plutonium, have shown less evidence of reaction. The greater reactivity of curium probably is to be attributed to the radioactivity of the isotope[2] Cm^{242} (equivalent to a power output of 1.2×10^{-4} watts/μg.), which, under some conditions, is sufficient to maintain the temperature of the sample substantially above that of its environment.

The trifluoride used for the reductions was prepared by precipitating Cm(III) in dilute nitric acid in a fluorothene microcone with an excess of hydrofluoric acid, washing the precipitate with dilute hydrofluoric acid, and drying the CmF_3 in platinum under a heat lamp. Pieces of the dry fluoride were then transferred to the inner crucible for reduction. When the quantities of curium were relatively large (*ca.* 10 μg.), the trifluoride was compacted in the bottom of the crucible by tamping with a quartz rod.

The conditions for reduction to usable metal were rather critical. Reduction at 1380° left the metal as a thin film adhering to the wall of the crucible. Reduction at about 1250° resulted in the formation of a cokey residue, indicating poor agglomeration of the metal. Reduction with barium vapor at 1275° for 45 seconds, followed by additional heating at 1100° for 45 seconds and a final heating at 960° for 20 seconds produced optimum results. In one such run on 12 μg. of CmF_3, reduction yielded a single 4 μg. spheroidal piece of metal. This piece was separated from the crucible, intact and free of slag or other residues.

The volume of the piece was estimated by measurement with a filar micrometer under about 200× magnification. The mass of the sample was

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(1) S. Fried and N. R. Davidson, THIS JOURNAL, **70**, 3539 (1948).

(2) The isotope used for this work was the 162-day Cm^{242}. The preparation and isolation of microgram quantities of Cm^{242} has been described by L. B. Werner and I. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.5 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

determined by weighing with a torsion microgram balance and the mass of curium by radiometric assay for Cm^{242}. The results of the last two measurements (which constitute a specific activity determination) indicated that the curium metal was pure, within the limit of error of the measurements (±5%).

From the mass and volume measurements the density of the metal was computed to be *ca.* 7. This is a surprisingly low value and perhaps is to be explained by the presence of a void in the piece of metal examined. Additional measurements of the density will be made as more curium becomes available.

This work was performed under the auspices of the U. S. A. E. C.

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RECEIVED SEPTEMBER 15, 1950

Oxidation of Aminopyridines to Nitropyridines[1]

BY RICHARD H. WILEY AND JOHN L. HARTMAN

The oxidation of aminopyridines to nitropyridines is an interesting reaction which has received but little attention since first reported by Kirpal and Bohm.[2,3] The reagent used is 30% hydrogen peroxide dissolved in 30% fuming sulfuric acid. Apparently only 2- and 4-aminopyridine[2,3] and 2-amino-5-bromopyridine[4] have been oxidized to the corresponding nitro compounds by this procedure. Yields of 55–75% were reported.

We wish to report the successful application of this oxidation procedure to the conversion of four 2-aminopicolines to the corresponding nitropicolines. Yields of 30–68% were obtained. Data for the compounds are recorded in the table. We have noted that at the end of the reaction period there is a color change from a dark-green to a lemon-yellow which can be used as a criterion for completion of the reaction.

When this oxidation procedure was applied to 3-aminopyridine, the product obtained was not 3-nitropyridine but 3,3′-azoxypyridine, m.p. 131–132°, previously obtained[5] by reduction of 3-nitropyridine.

Experimental

The oxidations of the 2-amino-3-methyl-, 2-amino-4-methyl-, 2-amino-5-methyl- and 2-amino-6-methylpyridine were all carried out in the same manner. The following procedure is typical.

2-Nitro-4-methylpyridine.—Three grams (0.028 mole) of the 2-amino-4-methylpyridine was dissolved in 10 ml. of concentrated sulfuric with the temperature being maintained at 10–20°. To this solution was added dropwise a mixture of 25 ml. of 30% hydrogen peroxide in 50 ml. of 30% fuming sulfuric acid while the temperature was again maintained at 10–20°. The temperature was held at 20° during a period of exothermic reaction, which varied from 1 to 3 hours, following the addition of the hydrogen peroxide mixture. The solution was kept at 25° for 48 hours after which it was added to 300 ml. of water with cooling and made very slightly basic with the dropwise addition of 50% sodium hydroxide solution while the temperature was maintained at 20–25°. The 2-nitro-4-methylpyridine was extracted using four 150-ml. portions of ether. Subsequent evaporation of the ether yielded 2.6 g., 68% of theoretical, of light yellow crystals which were recrystallized from an ethanol–water solution, m.p. 61–62°.

In similar experiments the crude yield of 2-nitro-5-methylpyridine was 30% while the crude yields of the other three nitropicolines varied from 60 to 68%. All were recrystallized from alcohol–water before analysis.

TABLE I

2-NITROPICOLINES

Position of methyl	M. p., °C.	Nitrogen, %	
		Calcd.	Found
3	43–44	20.28	19.93
4	61–62	20.28	20.06
5	94–95	20.28	20.03
6	113–114	20.28	20.08

3,3′-Azopyridine.—Three grams of 3-aminopyridine was treated according to the procedure described for the preparation of 2-nitro-4-methylpyridine. On evaporation of the ether and recrystallization from alcohol-water there was obtained 0.35 g., 11% of the theoretical yield, of 3,3′-azoxypyridine, m.p. 131–132°.

Anal. Calcd. for $C_{10}H_8N_4O$: N, 28.00. Found: N, 28.02.

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RECEIVED SEPTEMBER 14, 1950

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[1] The work described in this paper was carried out under contract NOrd 10804 between the Chemistry Department of the University of Louisville and the Navy Department, Bureau of Ordnance.

[2] Kirpal and Bohm, *Ber.*, **64**, 767 (1931).

[3] Kirpal and Bohm, *ibid.*, **65**, 680 (1932).

[4] Hertog, *et al.*, *Rec. trav. chim.*, **68**, 275 (1949).

[5] Friedl, *Monatsh.*, **34**, 763 (1913).

α-(*p*-Toluenesulfonamido)-phenylacetic and α-(Benzenesulfonamido)-phenylacetic Acids

BY RICHARD H. WILEY AND HOBERT L. DAVIS

Two previously undescribed sulfonyl derivatives of α-aminophenylacetic acid have been prepared and characterized. The procedure of McChesney and Swann[1] for making the *p*-toluenesulfonyl derivative of glycine was followed.

α-(*p*-Toluenesulfonamido)-phenylacetic Acid.—A solution of 6.31 g. of *p*-toluenesulfonyl chloride in 25 ml. of acetone was added slowly from a dropping funnel to a mechanically stirred, cooled solution of 5 g. of α-aminophenylacetic acid in 55 ml. of 2 *N* NaOH and 25 ml. of acetone. Water was added to dissolve the sodium salt that precipitated. After one hour the mixture was allowed to come to room temperature, and remain overnight. The acetone was removed *in vacuo* with a bath temperature of about 50°. The solution was cooled in an ice-bath and acidified to *p*H 1 with concentrated hydrochloric acid. The crystals were collected on a filter, washed with water and air-dried. The crude yield was 5.75 g., 57% of the theoretical. After recrystallization from hot water, the colorless crystals melted at 179–180° (uncorrected).

Anal. Calcd. for $C_{15}H_{15}O_4NS$: N, 4.59; neut. equiv., 305. Found: N, 4.33; neut. equiv., 304.

Benzenesulfonamidophenylacetic Acid.—The procedure described above was followed using 5.84 g. of benzenesulfonyl chloride and 5 g. of α-aminophenylacetic acid. There was obtained 6.35 g., 66% of the theoretical amount, of the sulfonamide. The crude product was recrystallized from hot water, m.p. 163–164° (uncorrected).

Anal. Calcd. for $C_{14}H_{13}O_4NS$: N, 4.82; neut. equiv., 290.3. Found: N, 4.72; neut. equiv., 290.4.

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RECEIVED SEPTEMBER 15, 1950

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[1] E. W. McChesney and W. K. Swann, Jr., THIS JOURNAL, **59**, 1116–1118 (1937).