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.

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