brass and coated by electrodeposition with the various metals.

The system was evacuated with a mercury diffusion pump in series with a rotary oil pump. A hydrogen pressure of approximately 0.5 mm. was maintained constant during each run as indicated by a McLeod gage.

In our measurements, the rise in temperature with time was recorded and the final steady-state temperature used in calculating results. Cobalt was chosen as the standard because of its high efficiency and resistance to poisoning. In each group of runs, the discharge was left on continuously and the cobalt cone and the others with which it was compared were introduced successively, each cone being introduced several times. The temperature rise relative to cobalt was thus obtained for each surface. Our results are summarized in Table I.

Freshly electroplated cones were used for each run. Although the absolute magnitude of ΔV varied from run to run, the values relative to cobalt remained quite reproducible. On the basis of the preceding results, the surfaces investigated may be assigned an order of activity as follows

$$\begin{array}{lllllll} \text{Pt} & & \text{Cu} & & \text{Zn} & & \\ \text{Co} & > & \text{brass} & > & \text{paraffin} & > & \text{Sn} \\ \text{Ni} & & \text{Fe} & & & & \\ & & \text{Cr} & & & & \\ & & \text{Cd} & & & & \end{array}$$

It was observed that the activity of a given cone tended to decline with time. This is probably attributable to progressive poisoning. The results were so reproducible that we believe the above relative efficiencies to be more accurate than those previously determined.[1,2,3]

(1) E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

(2) H. S. Taylor and G. I. Lavin, THIS JOURNAL, **52**, 1910 (1930).

(3) G. I. Lavin and W. F. Jackson, *ibid.*, **53**, 3189 (1931).

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Dinitration of *p*-Bromotoluene

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The simple nitration of *p*-bromotoluene has been studied in detail[1] but more vigorous nitration leading to the introduction of two nitro groups has not been hitherto reported. In the present study, the only product succcessfully isolated was 2,3-dinitro-4-bromotoluene, which was synthesized independently from 2,3-dinitro-4-aminotoluene. The 2,5-dinitro isomer was also prepared, but from 2,5-dinitro-4-aminotoluene. Both isomers and also the 3,5-dinitro isomer were reduced to the amines and acetylated.[2]

Experimental

The melting points given are uncorrected.

2,3-Dinitro-4-bromotoluene.—One ml. of *p*-bromotoluene was added dropwise to a vigorously shaken mixture of 4 ml. of 98% sulfuric acid and 2 ml. of 70% nitric acid, the temperature rising to 90° and then subsiding. The semisolid product was washed free of acid and crystallized from alcohol. About 200 mg. of colorless needles was obtained which melted at 129–130° after recrystallization from alcohol and which showed no depression in a mixed melting point determination with a sample prepared independently by the method described in the next paragraph.

One gram of 2,3-dinitro-4-aminotoluene[3] was slurried in 5 ml. of 98% sulfuric acid, cooled externally with ice, and 1 g. of sodium nitrite dissolved in 3 ml. of sulfuric acid was added slowly. The resulting slurry was stirred for one hour and a few crystals of sulfamic acid were then added. The slurry was added to a mixture of 25 ml. of 48% hydrobromic acid, 5 g. of cuprous bromide and 100 g. of ice. The mixture was allowed to stand in the cold for two days and was then poured into excess ice and filtered. The filter cake was leached with 50 ml. of hot alcohol, filtered and the filtrate evaporated to dryness. The residue was warmed on a steam-bath with 10 ml. of 70% nitric acid in which it dissolved. As soon as the evolution of nitric oxide ceased, the solution was diluted with a few ml. of water and cooled. The product formed colorless needles which when recrystallized from alcohol melted at 129°. The yield was about 200 mg.

Anal. Calcd. for $C_7H_5O_4N_2Br$: C, 32.2; H, 1.92; N, 10.72; Br, 30.6. Found: C, 32.0; H, 2.06; N, 11.0; Br, 30.6.

2,5-Dinitro-4-bromotoluene was prepared from 2,5-dinitro-4-aminotoluene[3] by the method described above. After two recrystallizations from alcohol it was obtained as straw-colored needles which melted at 111°.

Anal. Calcd. for $C_7H_5O_4N_2Br$: N, 10.72. Found: N, 10.9.

2,5-Diacetamino-4-bromotoluene was prepared by reducing the dinitro compound with tin and hydrochloric acid, followed by acetylation with acetic anhydride.[2] The product was twice recrystallized from alcohol and formed colorless needles which melted at 284°.

Anal. Calcd. for $C_{11}H_{13}O_2N_2Br$: C, 46.3; H, 4.56; N, 9.83; Br, 28.1. Found: C, 46.5; H, 4.70; N, 9.65; Br, 28.1.

2,3-Dinitro-4-bromotoluene failed to yield a crystalline derivative by this method.

3,5-Diacetamino-4-bromotoluene was prepared from 3,5-dinitro-4-bromotoluene[4] by the foregoing method. The product, recrystallized from alcohol, formed colorless needles which melted at 244.5–245°.

Anal. Calcd. for $C_{11}H_{13}O_2N_2Br$: C, 46.3; H, 4.56; N, 9.83; Br, 28.1. Found: C, 46.2; H, 4.64; N, 9.86, Br, 28.3.

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[1] (a) Shaw and Turner, *J. Chem. Soc.*, 1884 (1932); (b) Holleman, *Rec. trav. chim.*, **34**, 283 (1915).

[2] Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

[3] Page and Heasman, *J. Chem. Soc.*, **123**, 3235 (1923).

[4] Jackson and Ittner, *Am. Chem. J.*, **19**, 7 (1897).

CHICAGO, ILLINOIS
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meso-2,5-Dibromohexane

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The conversion of 2,5-hexanediol to 2,5-dibromohexane in 70–90% yields has previously been accomplished by treatment with fuming hydrobromic acid.[1,2,3] A distinctly more convenient procedure, which routinely gives better than 90% yields of 2,5-dibromohexane, involves treating the

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[1] Duden and Lemme, *Ber.*, **35**, 1335 (1902).

[2] Pace, *Arch. farmacol. sper.*, **42**, 167 (1926); *C. A.*, **21**, 1964 (1927).

[3] W. H. Florsheim, Ph.D. Thesis, University of California at Los Angeles, May, 1948.

glycol with phosphorus tribromide. Since the glycol is a mixture of stereoisomers, the dibromide produced is composed of the racemic and *meso*-forms; *meso*-2,5-dibromohexane is readily obtained from the crude reaction mixture by cooling.

Experimental

meso-**2,5-Dibromohexane.**—In a typical run, 118 g. (1 mole) of 2,5-hexanediol (Carbide and Carbon Chemicals Corp.) was placed in a 1-liter, 3-necked flask, fitted with a mercury-sealed, Hershberg-type tantalum stirrer, a thermometer, and a dropping funnel. The glycol was cooled to −5° and, while stirring, 600 g. (2.2 moles) of phosphorus tribromide was added at such a rate that the temperature did not rise above +5°. The dropping funnel was replaced by a reflux condenser carrying a drying tube and the mixture was allowed to come to room temperature overnight. It was then heated for one hour on a steam-bath after which it was cooled and poured onto about 1 kg. of ice. The organic layer was washed successively with water, 96% sulfuric acid, water, aqueous sodium bicarbonate, water and then dried over Drierite. Removal of the Drierite by filtration gave 232 g. (96% yield) of a pale yellow liquid. This crude 2,5-dibromohexane, if distilled, boils at 98-100° (19-20 mm.) and has $n^{20}\text{D}$ 1.4997-1.4999.

However, when the *meso*-dibromide was desired, the crude, pale yellow product was not distilled. Instead, it was cooled to −5°; the *meso*-dibromide readily crystallized and was isolated by filtration. The filtrate was then cooled to −50° and seeded with crystalline *meso*-dibromide. On standing several hours at −50° a second crop of crystalline *meso*-2,5-dibromohexane was obtained. No attempt was made to learn whether further cooling would lead to the crystallization of more *meso*-dibromide. In one run this mother liquor was distilled; b.p. 87-89° (12-13 mm.).

The combined crops of *meso*-dibromide (120 g.) were melted and then dissolved in an equal volume of hot methanol. Upon cooling, first to room temperature and then in an ice-chest, there was obtained 105 g. of *meso*-2,5-dibromide, m.p. 39°. A second recrystallization from methanol raised the melting point only slightly; the yield was 90 g. (36% based on the glycol) of colorless *meso*-2,5-dibromohexane which sinters at 38° and melts at 39.1 to 39.4°. Further recrystallization from methanol, carbon tetrachloride or glacial acetic acid did not raise the m.p.; lit. m.p. 30°,[4] 36°,[5] 38.2°,[5] 38-39°.[6]

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[4] Fried and Kleene, THIS JOURNAL, **63**, 2691 (1941).

[5] Wislicenus, *Ber.*, **34**, 2565 (1901).

[6] Demjanoff, *Chem. Ztg.*, **14**, 145 (1890); *Chem. Centr.*, **61**, I, 521 (1890).

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Attempted Reduction of Neodymium to the Divalent State

BY H. A. LAITINEN AND EVA BLODGETT

Holleck and Noddack[1] reported that a partial reduction of several rare earths to the divalent state could be achieved by shaking a concentrated rare earth sulfate solution with dilute strontium amalgam. It was presumed that the divalent sulfate was stabilized by occlusion in the precipitated strontium sulfate which was formed. As was to be expected from previously known behavior, europium, ytterbium and samarium were reduced to a considerable extent. In addition, a smaller degree of reduction was reported for scandium, gadolinium, cerium, praseodymium and neodymium.

Glockler, *et al.*,[2,3] were unable to confirm for neodymium and gadolinium the polarographic evidence of Noddack and Brukl[4] which indicated that all of the rare earths are capable of existence in the divalent state as the reduction product of the trivalent ion at the dropping mercury cathode. We have likewise been unable to obtain polarographic waves which would correspond to one-electron reductions of the trivalent ions of neodymium or gadolinium, either in the absence or presence of indifferent electrolytes.

It appeared of interest, with a view toward possible applications in rare earth separations, to reinvestigate the reduction of rare earth sulfates with strontium amalgam. Neodymium and ytterbium were chosen for study.

Preliminary experiments with blank solutions of sulfuric acid shaken with strontium amalgam showed that it was extremely difficult to separate the last traces of amalgam and/or mercury from the precipitate and from the supernatant liquid. After removal of the spent amalgam in a separatory funnel, followed by centrifugation, the suspended precipitate was allowed to stand with a solution of ferric ammonium sulfate and titrated with permanganate. Both the blank experiments and experiments with saturated neodymium sulfate showed a consumption to permanganate which would correspond to the production of 0.9 to 10.8% of reduced neodymium. Since no mention of blank experiments was made by Holleck and Noddack, who reported 4.6% of the coprecipitated neodymium to be in the reduced state, some doubt was cast on the validity of their observations.

Repeating the blank experiments under essentially the same conditions as described by Holleck and Noddack, but removing only about one-third of the precipitated strontium sulfate from the top of the centrifuged precipitate, it was possible to decrease the blank to a consumption of 0.5 ml. of 0.01 *N* permanganate. Under the same conditions, starting with 30 ml. of 0.1 *M* neodymium sulfate, a strontium sulfate precipitate which consumed only 0.4 ml. of 0.01 *N* permanganate was obtained. A similar experiment with 0.1 *M* ytterbium sulfate showed by gravimetric determination of the residual ytterbium in solution that 62% of the ytterbium had been carried down with the precipitate. Of this, 78% was in the reduced form as shown by treatment with ferric iron and titration with permanganate. The remainder had been carried down in the trivalent state or had been reoxidized before titration. This observation was in agreement with that of Holleck and Noddack, who reported that 80% of the coprecipitated ytterbium was in the divalent state.

It was also of interest to attempt to prove the presence of divalent rare earth ions in the solution during the amalgam reduction. For this purpose, the dropping mercury electrode was used as a potentiometric indicator electrode.[5] Divalent rare earth ions would be expected to produce an anodic current at all potentials more positive than the reduction potentials of the trivalent ions. Consequently, the "cathodic" condenser current of the dropping mercury electrode which occurs at all potentials more negative than that corresponding to the electrocapillary maximum of mercury should be compensated by

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[1] L. Holleck and W. Noddack, *Angew. Chemie*, **50**, 819 (1937).

[2] S. W. Rabideau and George Glockler, THIS JOURNAL, **70**, 1342 (1948).

[3] C. R. Estee and George Glockler, *ibid.*, **70**, 1344 (1948).

[4] W. Noddack and A. Brukl, *Angew. Chemie*, **50**, 362 (1937).

[5] H. A. Laitinen, T. Higuchi and Michael Czuha, THIS JOURNAL, **70**, 561 (1948).