

preparation were devised offering certain advantages over those given in the literature which invariably involve the use of clay as a starting material.<sup>5</sup>

The need for pure substances as phosphor bases eliminated such procedures.

#### Experimental

The following reagents were used: silicon dioxide from distilled silicon tetrachloride; aluminum oxide from sublimed aluminum chloride; sodium sulfide obtained by reduction with hydrogen of purified sodium sulfate; sodium carbonate purified by recrystallization.

An intimate mixture of these substances in the proportions  $3\text{Na}_2\text{CO}_3 + 3\text{Al}_2\text{O}_3 + 6\text{SiO}_2 + \text{Na}_2\text{S}$  was heated in nitrogen for fifteen hours at  $900^\circ$ . The pale green colored product was quite stable when ignited in air. This material, when heated in a stream of hydrogen sulfide for two hours at  $900^\circ$ , gave a yellow-green product which, upon ignition in air, yielded the deep blue ultramarine. X-Ray diffraction patterns revealed the characteristic cubic structure ( $a_0 = 9.0 \text{ \AA}$ ).<sup>6</sup>

By substituting  $2\text{NaCl}$  for  $\text{Na}_2\text{S}$  in the mixture, sodalite was obtained. The diffraction pattern was identical with that of natural sodalite reported by Barth.<sup>7</sup> It has a cubic structure similar to the ultramarines with unit cell dimension  $8.89 \text{ \AA}$ .

Sodalite was converted into a deeply-colored ultramarine by heating in a stream of hydrogen sulfide for two hours at  $900^\circ$  followed by heating in air. A qualitative test indicated substantially complete replacement of the chloride by sulfur.

A similar experiment, in which sodalite was heated in a stream of hydrogen and selenium vapor at  $1000^\circ$  followed by ignition in air gave a red-brown product also having the ultramarine structure.

(5) R. G. Woodbridge, *J. Chem. Ed.*, **26**, 552 (1949).

(6) F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 414.

(7) T. F. W. Barth, *Z. Krist.*, **83**, 409 (1932).

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## The Reduction of Phenolic $\beta$ -Nitrostyrenes by Lithium Aluminum Hydride

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The literature records the reduction of two  $\beta$ -nitrostyrenes to phenethylamines by lithium aluminum hydride.<sup>2</sup> We have found that this method affords an excellent route to phenolic phenethylamines. For the preparation of appreciable amounts of these compounds, none of the methods so far described<sup>3</sup> has been found suitable.

4-Hydroxy-3-methoxy-, 3-hydroxy-4-methoxy- and 2-hydroxy-3-methoxyphenethylamines were prepared from the corresponding  $\beta$ -nitrostyrenes and isolated as their picrates in yields of 80, 68 and 81%, respectively. The picrates were in turn converted to the stable hydrochlorides.

(1) Robert Earll McConnell Post-Doctorate Fellow.

(2) Nystrom and Brown, *THIS JOURNAL*, **70**, 3738 (1948); Hamlin and Weston, *ibid.*, **71**, 2210 (1949).

(3) (a) Kobayashi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **6**, 149 (1927); *C. A.*, **22**, 1345 (1928); (b) Buck, *THIS JOURNAL*, **55**, 3388 (1933); (c) Hahn and Rumpf, *Ber.*, **71**, 2141 (1938); (d) Hahn and Stiehl, *ibid.*, **71**, 2154 (1938).

In view of the amphoteric nature as well as the physical properties of the phenolic amines, this method of isolation was found very suitable.

The required  $\beta$ -nitrostyrenes were easily obtained by condensation of commercially available phenolic aldehydes with nitromethane using methylamine<sup>3d</sup> or ammonium acetate<sup>4</sup> as condensing agents.

#### Experimental<sup>5</sup>

**4-Hydroxy-3-methoxy- $\beta$ -nitrostyrene.**—A mixture of 7 g. of methylamine hydrochloride, 10 g. of sodium carbonate and 100 ml. of methanol was stirred well, filtered and added to a solution of 219 g. of vanillin and 85 ml. of nitromethane in 600 ml. of methanol. The solution was kept at room temperature in the dark for 72 hours and the  $\beta$ -nitrostyrene which crystallized out was collected and washed with cold methanol. The yield of yellow needles melting at  $166\text{--}168^\circ$  was 225 g. (81%); reported<sup>3d</sup> melting point,  $167\text{--}168^\circ$ .

**4-Hydroxy-3-methoxyphenethylamine.**—To a well-stirred mixture of 53 g. of lithium aluminum hydride and 2500 ml. of absolute ether was added by the Soxhlet extractor technique<sup>6</sup> 55 g. of 4-hydroxy-3-methoxy- $\beta$ -nitrostyrene over a period of 59 hours. Stirring and refluxing can be stopped and resumed at any time. The flask was cooled well and 3000 ml. of ice-cold 1.5 *N* sulfuric acid was added dropwise with stirring. The water layer was separated and its pH adjusted to 6 with solid lithium carbonate. The solution was heated to boiling, and the aluminum hydroxide which precipitated was filtered off with the aid of filter-cel; the clear, hot filtrate was mixed with a solution of 70 g. of picric acid in the minimum amount of hot ethanol. Upon standing overnight at room temperature, 89.2 g. (80%) of deep yellow needles of the picrate melting at  $194\text{--}197^\circ$  was obtained. Recrystallization from water raised the melting point to  $198\text{--}199^\circ$  (dec.); reported,<sup>3d</sup> m. p.,  $198\text{--}199^\circ$ .

A solution of 88 g. of the picrate in 2 l. of boiling water was mixed with 400 ml. of concentrated hydrochloric acid, the picric acid which precipitated on cooling was filtered, the filtrate was extracted with nitrobenzene and then with ether. The aqueous solution was concentrated under reduced pressure until crystals of the hydrochloride appeared. Thirty-six grams of tan crystals melting at  $211\text{--}213^\circ$  was collected. By evaporation of the filtrate to dryness and recrystallization of the residue from methanol-ethyl acetate, another 4 g. was isolated, making a total yield of 90%. The pure salt melted at  $213\text{--}214^\circ$ ; reported,<sup>3a</sup> m. p.,  $210\text{--}211^\circ$ . *Anal.* Calcd. for  $\text{C}_9\text{H}_{11}\text{ClNO}_2$ : N, 6.9. Found: N, 6.4.

The dibenzoyl derivative prepared from the hydrochloride melted at  $131\text{--}132^\circ$ ; reported<sup>3b</sup> m. p.,  $129^\circ$ .

**3-Hydroxy-4-methoxy- $\beta$ -nitrostyrene.**—This compound was prepared from 3.0 g. of isovanillin (Monsanto Chemical Co.) and 1.2 ml. of nitromethane by the same procedure as described above. The mixture was allowed to stand for 50 hours, and an 87% yield of yellow needles, m. p.  $156\text{--}159^\circ$ , was obtained. The product crystallized from methanol and melted at  $161\text{--}162^\circ$ . *Anal.* Calcd. for  $\text{C}_9\text{H}_9\text{NO}_4$ : N, 7.2. Found: N, 6.9. Hahn and Rumpf,<sup>3c</sup> who prepared this compound in 40.6% yield using potassium hydroxide as condensing agent, reported a m. p. of  $154^\circ$ .

**3-Hydroxy-4-methoxyphenethylamine.**—Using the same procedure as described above, 1.24 g. of 3-hydroxy-4-methoxy- $\beta$ -nitrostyrene was added over a period of 6 hours to 1.1 g. of lithium aluminum hydride in 150 ml. of ether. The yield of picrate melting at  $196\text{--}198^\circ$  (dec.) was 1.70 g. (68%). After one recrystallization from water the picrate melted at  $201\text{--}203^\circ$  (dec.); reported<sup>3e</sup> m. p.  $203\text{--}204^\circ$  (dec.).

(4) Raiford and Fox, *J. Org. Chem.*, **9**, 170 (1944).

(5) Microanalyses by Clark, Microanalytical Laboratory, Urbana, Ill. All melting points are corrected.

(6) Nystrom and Brown, *THIS JOURNAL*, **69**, 1197 (1947).

The hydrochloride was obtained from the picrate as colorless needles m. p. 206–207° (from methanol-ethyl acetate). *Anal.* Calcd. for  $C_9H_{14}ClNO_2$ : C, 53.1; H, 6.9. Found: C, 53.0; H, 6.8.

**2-Hydroxy-3-methoxy- $\beta$ -nitrostyrene.**—A solution of 5.0 g. of freshly distilled 2-hydroxy-3-methoxybenzaldehyde, 2.5 ml. of nitromethane and 2 g. of ammonium acetate in 20 ml. of glacial acetic acid was refluxed for 2 hours. The cooled dark mixture was poured into water and the gummy product allowed to crystallize. The crude solid was recrystallized from benzene, with the aid of Norit. The yield of yellow needles, melting at 115–122° was 2.32 g. (37%). The analytical sample melted at 129–130°. *Anal.* Calcd. for  $C_9H_9NO_4$ : N, 7.2. Found: N, 7.2. Using a methanolic solution of methylamine as condensing agent only 18% of the nitrostyrene was obtained after seven days. The reaction failed using potassium hydroxide as condensing agent.

**2-Hydroxy-3-methoxyphenethylamine.**—The yield of the picrate of the amine obtained from 1.0 g. of 2-hydroxy-3-methoxy- $\beta$ -nitrostyrene was 1.62 g. (81%), m. p. 168–170°; reported,<sup>3b</sup> m. p. 170°.

The hydrochloride crystallized from methanol-ethyl acetate as colorless plates, m. p. 177–178°; reported<sup>3b</sup> m. p. 175°.

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### Praseodymium and Neodymium Complexes with 8-Quinolinol-5-sulfonic Acid

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In a recent paper by Nakatsuka and Chang,<sup>1</sup> evidence is presented for the existence of higher oxidation states than three for praseodymium and neodymium in aqueous solution. They also present a method for the separation of these two neighboring rare earth elements. Because their findings would be of interest and significance, it was deemed important to repeat some of their experiments. Although we have not been able to confirm either the higher oxidation states or the separation method, there are constructive aspects to the chemistry involved that justify a brief note on it.

Nakatsuka and Chang subjected ammoniacal solutions containing 8-quinolinol-5-sulfonic acid and nitrates of praseodymium and neodymium to oxidation by the air and especially to anodic oxidation in a porous cup with a platinum anode. The solutions became dark reddish-brown in color; in the case of the more complete anodic oxidation, the solutions became opaque. For the separation, the oxidized mixtures were treated with sodium carbonate and glucose (reducing agent) and then heated, whereupon praseodymium(III) carbonate was reported to precipitate out, while the neodymium remained in solution.

In our own experiments an effort was made to confirm the separation method and to prepare, in solid form, the complex compounds that appear to exist in the mixtures indicated above.

(1) Y. Nakatsuka and T. Chang, *Acta Chimica Taiwanica*, **1**, 87 (1949).

### Experimental

**Reagents.**—Samples of the light blue  $Nd_2O_3$  and the jet black  $Pr_6O_{11}$ , each labeled 99% pure, were obtained from Research Chemicals, Incorporated, Burbank, California. Eastman Kodak Co. "white label" 8-quinolinol-5-sulfonic acid, recrystallized from 5% hydrochloric acid, was used throughout. All other chemicals were of Reagent Grade.

**Tests for Higher Oxidation States.**—To 100 cc. of 0.5 *N* ammonium hydroxide solution containing 1.5 g. of 8-quinolinol-5-sulfonic acid, was added 20 cc. of a solution containing 0.08 g. of praseodymium(III) as the nitrate; no precipitate formed. A similar blank solution containing no praseodymium was also prepared. On standing overnight exposed to the air both solutions became reddish-brown in color to about the same degree. Anodic oxidation for twenty minutes in a porous cup at 6 volts and 0.2 ampere caused both mixtures to become darkened to the extent of being opaque. No precipitate formed in either the test or blank solution.

It is evident that the color changes do not depend on the presence of praseodymium, and, therefore, no positive proof is provided at this stage that the praseodymium(III) was oxidized.

**Tests of Separation Procedure.**—Solutions containing praseodymium, neodymium and mixtures of the two were prepared and treated as described above. To each such opaque solution were added 10 g. of sodium carbonate and 3 g. of glucose and the resulting mixture was heated for one and one-half hours on a steam-bath.

In the case of praseodymium alone, it was found that praseodymium(III) carbonate would not precipitate quantitatively as claimed; from 10 to 50% of it remained in solution. The amount which precipitated was determined by converting the carbonate to the oxalate, by igniting the oxalate in a muffle furnace to the black oxide,  $Pr_6O_{11}$ , and by weighing this oxide. Also, it was not necessary to add glucose in order to precipitate part of the praseodymium carbonate. In the case of neodymium alone, it partially precipitated as the carbonate at the point in the procedure where praseodymium was supposed to precipitate quantitatively. The precipitates of neodymium(III) oxalate, on ignition, decomposed to form the light blue oxide,  $Nd_2O_3$ . In the case of the mixed sample, no semi-quantitative separation was observed. The oxides obtained from the ignition of the oxalates, which resulted from the conversion of the carbonate precipitate and from the filtrate from the carbonate precipitation, were the same shade of rust brown.

Thus the reported procedure for the separation of neodymium and praseodymium is impracticable, and constitutes no evidence for the existence, in solution, of higher oxidation states of these elements. Indeed, in view of recent work by Popov and Glockler<sup>2</sup> it appears that no stable compounds of neodymium in a higher oxidation state than three exist.

**Preparation of Complex.**—Our efforts to prepare solid samples of the praseodymium(III) derivative of the ammonium salt of 8-quinolinol-5-sulfonic acid were fruitless. The attempt to prepare this substance was made by adding a concentrated solution of  $PrCl_3$  to a concentrated solution of the ammonium salt of the sulfonic acid in an excess of ammonium hydroxide, and by further concentrating the resulting solution by gentle heating and evaporation. The solid obtained, when analyzed for praseodymium, nitrogen and sulfur, gave compositions which corresponded to no simple compound. It is likely that the difficulty was the same as that encountered by Jackson at the University of Illinois<sup>3</sup> in his successful attempts to prepare the lanthanum derivative of 8-quinolinol,  $La(C_9H_7NO)_3$ . This difficulty was the partial hydrolysis and decomposition of the desired derivative either in concentrated, supersaturated solutions, or by heating in the presence of water.

(2) Popov and Glockler, *This Journal*, **71**, 4114 (1949).

(3) University of Illinois, *N6-ori, Quarterly Progress Reports*, Nos. 10, p. 33; 11, p. 26; 12, p. 33; (1948–1949).