(twice the time theoretically required), the electrodes were removed and the catholyte and washings were collected. The isolation of the 2,3-bis-(*p*-aminophenyl)-2,3-butanediol dihydrochloride was accomplished by the method of Allen and Corwin,[1] with the exception that the temperature was kept under 50° (rather than 25°) in the evaporation of the final catholyte solution *in vacuo;* yield 10.2 g. (59%) of yellow-brown solid which decomposed slowly above 230°.

2,3-Bis-(*p*-aminophenyl)-2,3-butanediol.—Saturated aqueous potassium carbonate solution was added to a solution of 51.5 g. of the pinacol dihydrochloride in 300 ml. of water until the mixture was strongly alkaline. The solid precipitate was filtered and treated with hot acetone. The 2,3-bis-(*p*-aminophenyl)-2,3-butanediol separated from acetone as faintly yellow platelets, m.p. 239–242° dec. (reported[1] 248–249°), of analytical purity; yield 16.3 g. (40%).

THE CHEMICAL LABORATORIES
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

The Preparation of Samarium Metal[1]

BY E. I. ONSTOTT

RECEIVED JUNE 8, 1953

In a recent communication to the editor, Daane, Dennison and Spedding[2] described the preparation of samarium metal of at least 98% purity by reaction of samarium oxide with lanthanum metal. They also mentioned that barium had been tried as a reductant with little success. In this Laboratory relatively pure samarium metal has been produced by reaction of barium with anhydrous samarium(III) bromide. The reaction is carried out in a tantalum crucible[3] in an argon atmosphere by heating the mixture to a temperature of 1650–1700° for a period of about 20 minutes. During this heating period the samarium metal is collected in the bottom of the crucible and the excess barium is distilled out. The yield of metal is about 10 g. or 50% for a 50-g. batch of bromide. This technique of heating the charge to a high temperature to facilitate separation of the metal in the massive state has been used previously by Spedding, *et al.*, in the preparation of other rare earth metals.[4]

The purity of samarium metal prepared in this manner is believed to be greater than 99.5%. Spectrographic analysis showed the metal to contain: Li, Na, Mg, Ca, Mn, Fe, Cu, each less than 0.001%; Ba, Si, Sn, each less than 0.01%; Bi, 0.001–0.1%. Europium content was about 0.08%, since the samarium oxide used to make the anhydrous bromide contained this amount of europium oxide, as determined by a combination of gravimetric, colorimetric[5] and tracer analysis. No other rare earths were detected by spectrographic analysis. The samarium oxide as received from the Société de Produits Chimique des Terres Rares contained 1.5% calcium and 1.5% europium oxide. Purification was made by two electrolyses according to the method of McCoy,[6] followed by two oxalate precipitations and ignition to the oxide.

An experiment in this Laboratory confirms the report of Daane, Dennison and Spedding[2] that samarium metal is relatively volatile. When recasting samarium metal at about 1700° in an atmosphere of argon, approximately 1 g. of metal distilled to the lid of the crucible in a period of 5–10 minutes.

The density of three samples of samarium metal was determined by weighing in air, then weighing while suspended in acetylene tetrabromide. Density data are as follows: massive metal as made, 7.499 g./cc.; recast metal, 7.509 g./cc.; distilled metal, 7.495 g./cc. Accuracy of these data, which compare favorably to the value of 7.53 g./cc. obtained by Daane, Dennison and Spedding,[2] is believed to be ±0.005 g./cc.

Acknowledgment.—Some of the analyses were performed by Richard Wilhelm, O. R. Simi and F. H. Ellinger. Valuable suggestions were made by Dr. Henry Taube, Dr. E. R. Jette, Dr. R. D. Fowler and Dr. R. P. Hammond.

UNIVERSITY OF CALIFORNIA
LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS, NEW MEXICO

---

[1] This work is a contribution from the Chemical and Metallurgical Research Division of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico, under the auspices of the Atomic Energy Commission.

[2] A. H. Daane, D. H. Dennison and F. H. Spedding, THIS JOURNAL, **75**, 2272 (1953).

[3] A. H. Daane, *Rev. Sci. Instruments*, **23**, 245 (1952).

[4] F. H. Spedding and A. H. Daane, THIS JOURNAL, **74**, 2783 (1952).

[5] T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

[6] H. N. McCoy, THIS JOURNAL, **63**, 3432 (1941).

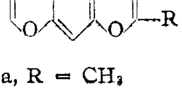
Furochromones and -Coumarins. VIII. Action of Hydrazine Hydrate and Hydroxylamine on Khellin, Khellol and Visnagin

BY ALEXANDER SCHÖNBERG AND MAHMOUD MOHAMED SIDKY

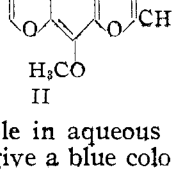
RECEIVED APRIL 10, 1953

The action of hydrazine hydrate on 2-methylchromone has been studied by Koenigs and Freund,[1] and on chromone itself by Baker, Harborne and Ollis.[2] Both groups of researches agree that the reaction products are pyrazole derivatives and not hydrazones of the chromones in question as previously believed. In the case of chromone itself, the product is 5(3)-*o*-hydroxyphenylpyrazole (IIId or IVd).

We have investigated the action of hydrazine hydrate on visnagin (Ia), khellol (Ib) and khellin (II), and believe that the reaction products are the pyrazole derivatives IIIa, IIIb and IIIc or IVa, IVb and IVc, respectively.



Ia, R = CH_3
Ib, R = CH_2OH



II

These substances are soluble in aqueous alkali, and their alcoholic solutions give a blue color with aqueous ferric chloride solution, and with titanium chloride a deep orange color is developed. From IIIa and IIIc—each containing one active hydrogen in the phenolic hydroxy group and one active hydrogen atom attached to a nitrogen atom—dibenzoyl derivatives were obtained when they were treated with benzoyl chloride (Schotten–Baumann).

---

[1] E. Koenigs and J. Freund, *Ber.*, **80**, 143 (1947).

[2] W. Baker, J. B. Harborne and W. D. Ollis, *J. Chem. Soc.*, 1303 (1952).