[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XLV. Preparation of Rare Earth Amalgams by Displacement[1]

BY D. H. WEST WITH B. S. HOPKINS

Rare earth metal amalgams have been prepared by direct combination[2] and by electrolysis[3] in non-aqueous solvents using a mercury cathode. Amalgams prepared electrolytically have been decomposed thermally to obtain metallic lanthanum, cerium and neodymium.[4]

Barium amalgam is conveniently prepared[5] by allowing sodium amalgam to react with aqueous barium chloride solution. Barium is quite closely related to the rare earths, being slightly more active. Since such a method might have advantages over the electrolytic preparation, an investigation of this possibility was entered upon to find out whether displacement can be used and if so to ascertain the most favorable conditions for the reaction.

Experimental

Preparation of Anhydrous Chlorides.—Anhydrous chlorides of the rare earth materials were prepared by the method of Reed[6] with some changes. The dry oxides were first ground in a large mortar with twice the calculated weight of ammonium chloride. Instead of heating this mixture in open casseroles and stirring by hand it was found convenient to carry out the operation in a Pyrex flask. This was slowly rotated at an angle of thirty degrees with the horizontal in an air-bath which was heated to 225–250° until the reaction was complete. The removal of excess ammonium salts was carried out by heating to 300–320° in the evacuated Pyrex apparatus described by Reed.

In this way the anhydrous chlorides of neodymium, a didymium mixture, samarium and yttrium were prepared without difficulty, the product in most cases being free from oxide or basic chloride as shown by complete solubility in water. Cerium dioxide reacted much more slowly with the ammonium chloride but by adding a three or four-fold excess of the latter and continuing the reaction for ten to twelve hours it was possible to prepare a product containing only a small amount of unconverted oxide.

Preparation of Amalgams.—It was found that sodium amalgam would react with the rare earth chlorides in alcohol solution forming the rare earth amalgam according to the equation

$$3NaHg_x + RCl_3 \longrightarrow 3NaCl + RHg_y$$

The sodium chloride is precipitated as is also some rare earth chloride. The displacement reaction begins rapidly forming an amalgam which contains a preponderance of rare earth metal. Although the reaction goes nearly to completion there is always a trace of sodium left in the amalgam. After a time there is a tendency for the amalgam to decompose, both sodium and rare earth metals resulting. Analysis of the amalgams was carried out by allowing them to decompose in air for three to five days and treating the residue with dilute hydrochloric acid. The soluble material was filtered off, evaporated and converted to the nitrate. From this solution the rare earth was precipitated as the oxalate and ignited to the oxide. The filtrate from the latter operation was fumed down with sulfuric acid and the sodium was weighed as the sulfate after ignition in platinum to red heat.

The sodium amalgams used were prepared in pulverized form by direct combination of the metals. Concentrations of 2–2.5% by weight of sodium gave the best results. More concentrated amalgams were so hard that they reacted very slowly with the rare earth chlorides. The sodium amalgam was agitated with the alcohol solutions by means of a stirrer driven by compressed air. The containers used were either large test-tubes or Erlenmeyer flasks.

With cerium, neodymium and "didymium" mixture, one hour was sufficient time to allow for the formation of good amalgams containing 3 to 3.5% rare earth metal and a small amount of sodium. The reaction was slower in the case of yttrium, two to three hours of stirring being required. Yttrium amalgams and amalgams of a mixture containing about 70% yttrium with erbium and other yttrium group earths were prepared in concentrations of 2 to 2.5% rare earth metal. Results of typical runs are given in Table I. In all cases a three to four fold excess of the rare earth salt was used.

TABLE I

Material	Time, min.	% Na in starting amalgam	Wt. Hg recovered, g.	Metals in final amalgam % R. E. metal	% Na
Didymium	21	1.24	105.45	1.74	0.274
Didymium	35	1.63	16.72	2.20	.038
Didymium	60	2.68	6.83	3.38	.141
Didymium	40	2.50	27.07	3.15	.085
Didymium	20	19.60	5.31	3.20	.500
70% Yttrium	60	2.50	23.71	2.58	.342
Yttrium	90	1.76	35.03	1.56	.271
Cerium	45	2.50	22.52	3.40	.120
Neodymium	35	1.88	25.42	3.20	.370

Rare earth amalgams have been prepared electrolytically from water solution. However, no success was encountered by the authors in attempting to carry out the displacement reaction in water solution or in alcohol solutions containing appreciable amounts of water. Methyl

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(1) An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1935.

(2) Müller, *Monatsh.*, **53–54**, 215 (1929).

(3) Audrieth, Jukkola, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931).

(4) Jukkola, Audrieth and Hopkins, *ibid.*, **56**, 303 (1934).

(5) Böttger, *J. prakt. Chem.*, **1**, 305 (1834).

(6) J. B. Reed THIS JOURNAL, **57**, 1159 (1935).

alcohol was satisfactory but best results were obtained with absolute ethyl alcohol saturated with the rare earth salt.

It was found best to cool the reaction tube with tap water since heat is developed by the reaction and at the higher temperature the tendency toward decomposition of the amalgam increases.

Potassium amalgams reacted with the anhydrous rare earth chlorides similarly to the sodium amalgams but were not as satisfactory. Barium amalgam gave partial displacement of the cerium group elements but did not react at all with the yttrium chlorides.

Yttrium amalgam was readily decomposed by heating in an evacuated Pyrex distilling bulb, the product being a pyrophoric powder which contained a small amount of mercury. Attempts to obtain yttrium metal entirely free from mercury have thus far been unsuccessful. The removal of all the mercury from the amalgams of the cerium group metals was successfully accomplished by placing the amalgams in an alundum crucible which had a lining of rare earth oxides and heating in a steel vacuum chamber by means of an electric furnace.

Summary

1. Amalgams of cerium, neodymium, didymium and yttrium have been prepared by displacement from the alcohol solution of their chlorides by sodium amalgam.

2. The most successful runs were made by suspending powdered sodium amalgam, containing 2–2.5% sodium, in a saturated alcoholic solution of the rare earth chlorides. The mixture was thoroughly agitated; the time required varied with the rare earth used.

3. This method takes much less time than the electrolytic method and gives a considerably more concentrated amalgam in the case of yttrium. The amalgams always retain a trace of sodium.

4. Metals of the cerium group were obtained free from the mercury by heating their amalgams in an evacuated chamber. This method did not yield yttrium which was entirely free from mercury.

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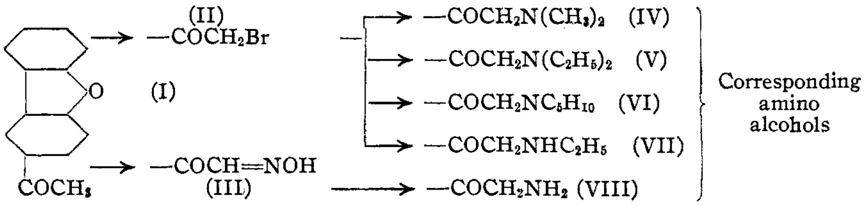
Amino Alcohols Derived from Dibenzofuran[1]

BY ERICH MOSETTIG AND RICHARD A. ROBINSON

The structural similarity of dibenzofuran to 4,5-phenanthrylene oxide has led us to the study of dibenzofuran derivatives[2] as a part of our search for morphine substitutes. The present communication deals with dibenzofuran alkamines containing the characteristic side chain —CHOH—CH_2—NR_2; these compounds were selected for comparison with amino alcohols of the phenanthrene series which have been found to resemble morphine somewhat in physiological action.[3] Such comparison of dibenzofuran and phenanthrene analogs may yield information as to whether the phenanthrene nucleus contributes an essential part to the total physiological action of morphine, or whether it can be replaced by another polynuclear system.

Starting from the known 2-acetyldibenzofuran, the synthesis of the alkamines was accomplished as outlined in the diagram.



The tertiary amino ketones IV, V and VI were prepared by a method similar to that used for the synthesis of their respective phenanthrene analogs.[3] The primary amino ketone VIII was obtained by reduction of the isonitroso compound III according to the method of Hartung and Munch.[4]

The exchange of the bromine atom in II with ethylamine yields only about 30% of the expected ethylamino ketone VII. The yield of the corresponding monomethylamino ketone does not exceed 5%. In the latter case a small amount of

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(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) Mosettig and Robinson, THIS JOURNAL, **57**, 902 (1935).

(3) (a) Mosettig and van de Kamp, *ibid.*, **55**, 3448 (1933); (b) unpublished results by Eddy and co-workers, University of Michigan.

(4) Hartung and Munch, *ibid.*, **51**, 2262 (1929).