which is entirely different from Pratesi's diagram; it shows log k about 0.2 at 625 mμ and falls off to log k about -0.5 at 470 mμ and log k about -0.25 at 800 mμ without reaching a minimum. The solvent used is not indicated.

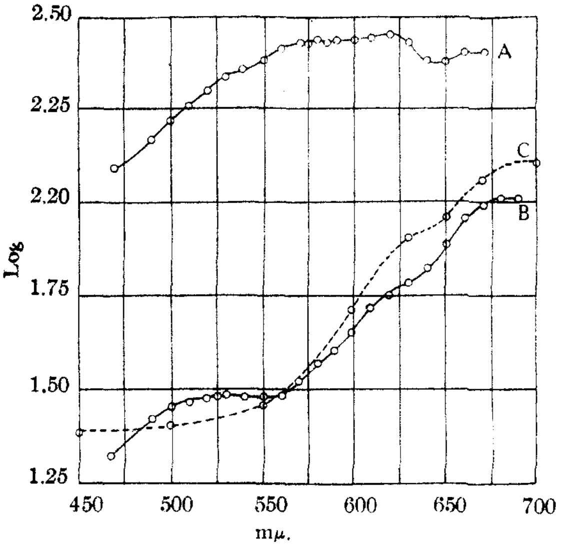

Fig. 1.—A, Pyrrole blue A, 50.94 mg. per liter of glacial acid; B, pyrrole blue B, 15.5 mg. per liter of glacial acetic acid; C, 2,3-dimethyl pyrrole blue in pyridine calculated from Pratesi's data.

The absorption curves of pyrrole blue A and B are not known since Pratesi measured only homologous substances of these dyestuffs and Grassmann and v. Arnim's curve differs so much from Pratesi's that it is improbable that it belongs to the B compound. A determination of the spectra of pyrrole blue A and B seemed therefore indicated.

Pyrrole blue B was prepared according to Liebermann and Häse[2] and dissolved in glacial acetic acid. The extinction was measured in a Hilger-Nutting spectrophotometer[6] with glacial acetic acid as a compensating liquid. The results are given in Fig. 1 curve B. Measurements in alcoholic hydrochloric acid gave a very similar picture. The curve resembles Pratesi's diagram for the homologous pyrrole blues (see curve C).

Both the acetic acid and the alcoholic solution are very unstable. They begin to change their spectrum after a few hours; the change continues through several days. The maximum at 520 mμ increases to log k about 1.9 while the maximum at 680 mμ disappears completely; no minimum could be observed in the visible range. The material represented in spectrum B seems therefore to contain some of the decomposition product.

Pyrrole blue A was prepared according to Pratesi and Zanetta[7]; these authors have pointed out that pyrrole blue A is not an oxidation product or derivative of pyrrole blue B but the result of a completely different reaction between pyrrole and isatin. Its absorption spectrum measured in glacial acetic acid in the Hilger-Nutting spectrophotometer is given in curve A Fig. 1. It confirms the assumption that the structure of pyrrole blue A is different from that of the B compound. Also the solutions of dyestuffs A are extremely unstable.

---

(6) The author is greatly indebted to the Chemistry Department of the University of Michigan for the permission of using this instrument and to Dr. F. F. Blicke for the supply of pyrrole.

(7) Pratesi and Zanetta, *Atti Acad. nazion. Lincei, Ren.*, [6] **22**, 159 (1935).

SAN GERMAN, PUERTO RICO RECEIVED JANUARY 7, 1944

The Basic Nitrite of Lanthanum

BY G. R. SHERWOOD

In 1914 Holden and James[1] reported that they got unusually rapid separation of yttrium from the other yttrium earths by the method of fractional precipitation with sodium nitrite. The method has been used and improved by other workers, but there seems to be no record of a quantitative study of the precipitate nor of the most favorable conditions under which it should be produced.

The lanthanum material used for these experiments showed only very faint spectral lines of praseodymium and neodymium. In addition it contained traces of cerium and manganese. It was therefore of satisfactory purity.

Some of the lanthanum solutions used were chlorides, others were nitrates. Either salt seemed to work about equally well. The lanthanum basic nitrite was prepared from these approximately 0.05 molar lanthanum solutions using the method as modified by Sherwood and Hopkins.[2]

The precipitated basic nitrite liberated iodine from hydroiodic acid, reduced acidified permanganate, and behaved in general as one would expect a nitrite to behave. All but the merest trace of sodium salts could be removed from it by simply washing it with water. The basic nitrite was surprisingly stable toward heat, at least up to approximately the boiling point of concentrated sulfuric acid.

It was found that the speed of precipitation increased with increased nitrite ion concentration, being too slow in half molar nitrite solution but satisfactory if the nitrite ion concentration was two molar.

Attempts were made to dry the first precipitates to constant weight in an oven at 110°. This was difficult to accomplish and the results did not seem significant. So subsequent precipitates were analyzed for La_2O_3 and N_2O_3 and the ratio of La_2O_3 to N_2O_3 determined for each sample.

A study was made to see whether the composi-

---

(1) Holden and James, THIS JOURNAL, **36**, 1418 (1914).

(2) Sherwood and Hopkins, *ibid.*, **55**, 3117 (1933).

tion of the precipitate was affected by the concentration of nitrite ion. A solution of lanthanum chloride was divided into three equal parts, one being made 0.5 molar, the second 1 molar, and the third 2 molar with sodium nitrite. There was no appreciable difference in the analyses of the precipitates produced from the three parts. Within these limits of nitrite ion concentration (0.5 molar to 2 molar) the precipitates consistently showed a molar ratio of La_2O_3 to N_2O_3 of between 1.01 and 1.02 for the purest lanthanum material. However, if the nitrite ion concentration became much less than 0.5 molar, a precipitate could be produced by boiling which contained almost no nitrite. This presumably was lanthanum hydroxide.

Methods were tried for the production of colloidal precipitates which have bothered previous workers so much. One method was the addition of a large excess of sodium chloride along with the sodium nitrite. This did not produce a colloid. However, the addition of a high concentration of sodium nitrite to a solution containing practically no free acid did produce a precipitate on boiling which was colloidal. In this case it was found that the initial *p*H had been allowed to become too high and that it fell as boiling started. The lanthanum solution should have a *p*H of approximately 5 before the sodium nitrite solution is added. Both the solutions should be at or only slightly above room temperature when they are mixed.

Using the above procedure the basic nitrite starts to precipitate from a 0.05 molar lanthanum solution at a *p*H of approximately 6.3 as compared to *p*H of approximately 8.3 required to precipitate its hydroxide.

This study indicates that a basic nitrite of lanthanum of very desirable properties can consistently be obtained by making a very faintly acidic solution of lanthanum chloride from 0.5 molar to 2 molar with sodium nitrite and subsequently boiling.

DEPARTMENT OF CHEMISTRY
WAYNE UNIVERSITY
DETROIT, MICHIGAN

RECEIVED MARCH 20, 1944

2,3-Dihydroxypropyl *n*-Dodecyl Ether

BY OLIVER GRUMMITT AND ROBERT F. HALL[1]

Although a number of the lower aliphatic and aromatic alpha mono-ethers of glycerol have been described,[2] the higher aliphatic derivatives are mentioned only briefly in the patent literature.[3] In order to obtain a typical member of this class of compounds the preparation of 2,3-dihydroxypropyl *n*-dodecyl ether (α-glycerol lauryl ether) was undertaken. Epichlorohydrin and excess lauryl alcohol in the presence of anhydrous ferric chloride reacted at 160° to give a 39% yield of 3-chloro-2-hydroxypropyl *n*-dodecyl ether. The corresponding epoxy compound (glycidol ether) was obtained in a 74% yield by removal of the units of hydrogen chloride with sodium hydroxide in *n*-butyl ether as a diluent. Hydrolysis of this intermediate to the glycerol ether, 2,3-dihydroxypropyl *n*-dodecyl ether, was unexpectedly slow—practically no hydrolysis occurred with excess dilute hydrochloric acid after eight hours of refluxing, but at 160° in a closed tube the hydrolysis was complete in eight hours.

2,3-Dihydroxypropyl *n*-dodecyl ether is a wax-like solid melting at about 20°. As do other 1,2-glycols, it undergoes quantitative oxidation with lead tetraacetate.[4] The rate of oxidation, however, is low in comparison with that of a glycerol mono-ester; for example, α-monostearin is quantitatively oxidized in six hours at 50°,[5] but the ether required more than twenty-one hours at the same temperature.

Experimental

3-Chloro-2-hydroxypropyl *n*-Dodecyl Ether.—A mixture of 9.7 g. (0.1 mole) of Eastman Kodak Co. epichlorohydrin, 37.2 g. (0.2 mole) of lauryl alcohol (E. K., m. p. 23–24°) and 0.4 g. of anhydrous ferric chloride was heated in a sealed, glass-lined metal tube for eighteen hours in an oil-bath held at 160°. The reaction mixture was transferred to a Claisen flask with a small amount of ether for rinsing, and the ether distilled on the steam-bath. The residue was distilled at 1–2 mm. pressure to give 10.9 g. at 114–150°, consisting mostly of unreacted epichlorohydrin and lauryl alcohol, 11.4 g. of product at 150–160° (39% of the theoretical yield), and a residue of 6.2 g. Redistillation gave 157° (1 mm.) as the approximate boiling point. The ether was a water-white liquid of faint odor showing $n^{25}\mathrm{D}$ of 1.4525.[6]

In the absence of the ferric chloride catalyst the yield was only 16%. With equimolar quantities of reactants and in the presence of 1% of catalyst the yield was 27%. A 2/1 mole ratio of epichlorohydrin to alcohol and in the presence of the catalyst raised the yield to 35%, and reversing the relative quantities taken to a mole ratio of 1/2 gave a 39% yield, as described above.

2,3-Epoxypropyl *n*-Dodecyl Ether.—A mixture of 12 g. (0.043 mole) of 3-chloro-2-hydroxypropyl *n*-dodecyl ether, 3.9 g. (0.098 mole) of pulverized sodium hydroxide, and 36 cc. of anhydrous *n*-butyl ether was heated under reflux with frequent shaking on the steam-bath for one hour. The pulverized sodium hydroxide was made from the pellets with a mortar and pestle and a few cc. of *n*-butyl ether to protect the surface against carbonate formation. The *n*-butyl ether was dried by distilling the technical grade to give the 138–141° fraction. After heating, the reaction solution was transferred to a Claisen flask with anhydrous ether for rinsing, and distilled: 7.7 g. at 132–135° (1–2 mm.) were collected; $n^{20}\mathrm{D}$ 1.4434; 74% yield.

Anal. Calcd. for $C_{15}H_{30}O_2$: C, 74.25; H, 12.47. Found: C, 74.61; H, 12.06.

Experiments with no diluent gave much lower yields. Longer reaction time and/or higher temperature likewise gave lower yields (10–55%). When the yield of ether is

---

[1] Present address: United Co-Operatives, Inc., Alliance, Ohio.

[2] For example, the α-ethyl ether by Nef, *Ann.*, **335**, 232 (1904), and the α-phenyl ether by Lindeman, *Ber.*, **24**, 2146 (1891).

[3] Henkel and Co., French Patent 751,923, Sept. 12, 1933; *C. A.*, **28**, 777 (1934).

[4] Criegee, *Ber.*, **64**, 260 (1931).

[5] Hilditch and Rigg, *J. Chem. Soc.*, 1774 (1935).

[6] Henkel and Co., French Patent 744,749, April 26, 1933; *C. A.*, **27**, 4242 (1933).