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.

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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 waxlike 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 $n^{25}D$ 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; $n^{20}D$ 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

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[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).

decreased, the amount of material boiling much higher than the ether is increased.

2,3-Dihydroxypropyl *n*-Dodecyl Ether.—A mixture of 3.6 g. (0.015 mole) of the 2,3-epoxypropyl *n*-dodecyl ether and 5.4 g. (0.3 mole of water) of 5% sulfuric acid was heated in the sealed tube at 160° for eight hours. The crude product was rinsed from the tube with 20-30 cc. of ether, neutralized with solid potassium carbonate and the ether layer separated. The aqueous layer was extracted with two 10-cc. portions of ether and the combined ether solutions were distilled on the steam-bath and finally under 15 mm. pressure to remove the last traces of ether and water. The residue weighed 3.0 g., 78% of the theoretical yield; $n^{20}_{\rm D}$ 1.4534. This compound is a wax-like solid melting about 20°, insoluble in water, soluble in methanol, ethanol, ether, acetone, carbon tetrachloride and benzene.

Preliminary hydrolysis experiments with excess water at 100° for twelve hours, 1% hydrochloric acid at 100° for eight hours, and 1% hydrochloric acid at 130° for eight hours all gave incomplete hydrolysis. The change in refractive index in going from the glycidol ether to the glycerol ether, 1.4434 to 1.4534 at 20°, was used to follow the course of the hydrolysis.

Anal. Calcd. for $C_{15}H_{32}O_3$: C, 69.12; H, 12.38. Found: C, 69.46; H, 12.39.

Samples of the ether were quantitatively oxidized at 50° with lead tetraacetate in glacial acetic acid solution according to the procedure of Criegee.[4] The following results are expressed as percentage of ether in the sample: six hours reaction time, 38.7%; twelve hours, 70.2%; twenty-one hours, 91.2%. By extrapolation of these data it appears that twenty-eight to thirty hours would be required for complete oxidation.

Reaction Tube.—Figure 1 shows a simple, convenient pressure tube made from steel tubing $1^3/_{16}''$ o. d., $^{15}/_{16}''$ i. d., and 15″ in length, closed at one end by a welded steel disk. The open end is machined flat so that a copper-asbestos gasket held in place by a metal plug (2) and threaded cap (3) will make a gas-tight seal.[7] A 22 mm. o. d. glass tube closed at one end is used as a glass liner.

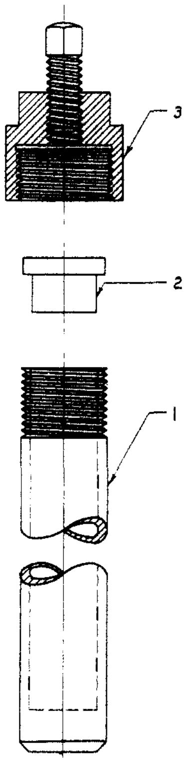

Fig. 1.—Metal bomb tube.

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[7] More complete descriptions of this type of closure are given in "A High Pressure Gas-Compression System," Dilley and Edwards, Circular 61, U. S. Dept. of Agriculture, Jan., 1929; and in J. H. Perry, "Chemical Engineers' Handbook," 2nd ed., McGraw-Hill Book Co., New York, 1941, p. 2181.

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RECEIVED JANUARY 24, 1944

Furfuryl Furoate by Condensation from Furfural

BY ERIK R. NIELSEN

Furfuryl furoate has been prepared by the condensation of furfural in the presence of sodium furfurylate. Previous attempts to carry out this condensation have been unsuccessful and have been cited to show a breakdown in the analogy between benzaldehyde and furfural.[1] The author has modified the method described for benzyl benzoate by Kamm and Kamm[2] to the extent that the condensing agent is prepared and the reaction carried out in the presence of refluxing benzene, whereby the danger of forming the ether rather than the ester is eliminated.

Experimental.—Eighteen grams of metallic sodium was added portionwise to a mixture of 250 g. of distilled furfuryl alcohol and 750 cc. of benzene, contained in a 3-liter flask (reflux condenser). After the condensing agent had been prepared, 1350 g. of distilled furfural was added through the reflux condenser at a rate so as to maintain refluxing by the heat developed by the reaction. The reaction mixture was washed with salt brine and distilled. The ester was recovered as a fraction boiling 121° (1.5 mm.) (77.8%). The solidified ester melted at 18.5° (uncor.) and did not convert to the allotropic form melting at 27.5° which has been reported to be the stable form by Zanetti.[1] The liquid ester showed a specific gravity d^{25}_{25} of 1.2384 and a refractive index $n^{20}_{\rm D}$ of 1.5280. An analyses of the ester showed

	Acidity as furoic acid, %	Saponification equivalent	Carbon,[3] %	Hydrogen,[3] %
Calcd.		192	62.48	4.19
Found	0.23	195	62.25	4.32

The ester was characterized further by saponification to yield furfuryl alcohol and furoic acid.

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[1] H. Gilman and Clarence C. Vernon, THIS JOURNAL, **46**, 2578 (1924); J. E. Zanetti, *ibid.*, **47**, 1452-1453 (1925).

[2] O. Kamm and W. F. Kamm, "Organic Syntheses," Coll. Vol. I, pp. 99-101.

[3] These analyses are by Dr. T. S. Ma, University of Chicago.

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RECEIVED APRIL 7, 1944

The Preparation of Potassium Triphenylmethide and its Use in Certain Condensations[1]

BY ROBERT LEVINE, ERWIN BAUMGARTEN AND CHARLES R. HAUSER

Sodium triphenylmethide is a useful reagent for the acylation[2] and alkylation[3] of esters and for the carbonation and carbethoxylation of esters[4] and ketones.[5] The sodium triphenylmethide has been prepared from triphenylchloromethane and sodium amalgam. While this method is quite satisfactory, there would be an advantage in preparing sodium triphenylmethide from triphenylmethane which would be regenerated when the reagent is used to effect condensations.

Sodium triphenylmethide is readily prepared from triphenylmethane and sodium amide in liquid ammonia[6] but the reagent is destroyed[7]

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[1] Paper XXVII on "Condensations"; paper XXVI, THIS JOURNAL, **66**, 1220 (1944).

[2] See especially Hauser and Hudson, "Organic Reactions," Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter IX.

[3] Hudson and Hauser, (a) THIS JOURNAL, **62**, 2457 (1940); (b) **63**, 3156 (1941).

[4] Baumgarten and Hauser, *ibid.*, **66**, 1037 (1944).

[5] Baumgarten, Levine and Hauser, *ibid.*, **66**, 862 (1944).

[6] Kraus and Kahler, *ibid.*, **55**, 3538 (1933).

[7] Kraus and Rosen, *ibid.*, **47**, 2739 (1925).