

3. A rapid method for the separation of benzene is proposed. the ortho and para isomers of aminoethyl-

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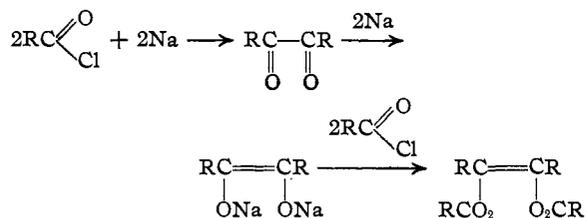
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Action of Sodium upon High Molecular Weight Fatty Acid Chlorides

BY A. W. RALSTON AND W. M. SELBY

Previous work upon the action of sodium with acid chlorides has been confined to chlorides of aromatic and low molecular weight aliphatic acids. Recently Pearl, Evans and Dehn¹ have shown that sodium reacts with benzoyl chloride in anhydrous ether to give ethyl benzoate, and that potassium reacts with benzoyl chloride in anhydrous xylene to give benzoic anhydride. Münchmeyer,² Klinger and Schmitz,³ and Basse and Klinger⁴ obtained the dibutyrate of 4-octene-4,5-diol by the action of sodium upon butyryl chloride in anhydrous ether. In view of the decrease in chemical activity with increase in molecular weight, the action of the high molecular weight fatty acid chlorides with sodium in ether is of interest.

Lauroyl, myristoyl, palmitoyl and stearoyl chlorides react smoothly at the boiling point of ether to give the corresponding diesters of the unsaturated diols in substantial yields. The failure to form ethyl esters of the corresponding acids, which would require scission of the ether, is noteworthy. Using stearoyl chloride and sodium as an example, the formation of the diesters of the diols can be explained as follows



Experimental

Preparation of the Acid Chlorides.—Stearic acid (586 g., 2 moles), m. p. 67–70°, was placed in a three-necked flask fitted with a dropping funnel, reflux condenser, mechanical stirrer and thermometer. Thionyl chloride (285.5 g., 2.4 moles) was then added over a period of two and one-half hours and the mixture heated at 75° for two hours. The temperature was then increased to 90°

and the heating continued for an additional two hours. The excess thionyl chloride was then removed under a vacuum and the product fractionally distilled. An 81% yield of stearoyl chloride boiling at 200–215° at 13–15 mm. was obtained.

The acid chlorides of lauric, myristic and palmitic acids were prepared in a similar manner. Approximately 80% yields were obtained with the following boiling ranges: lauroyl chloride, 146–150° at 16–17 mm.; myristoyl chloride, 175–176° at 16–17 mm.; and palmitoyl chloride, 191–194° at 14–15 mm.

Preparation of the Dilaurate of 12-Tetracosene-12,13-diol.—Sodium (27.5 g., 1.2 moles) was pressed as wire into a two-liter three-necked flask containing 1 liter of sodium dried ether. The flask was fitted with a reflux condenser, stirrer, thermometer and dropping funnel. Lauroyl chloride (218 g., 1 mole) dissolved in 200 cc. of dry ether was then added over a period of four hours. Stirring was not started until the addition of the lauroyl chloride was completed. The mixture was then refluxed and stirred for ten hours.

The sodium chloride and unreacted sodium were filtered from the ether solution and the filter washed with ether. The ether was then removed by distillation. After four crystallizations from a 3:1 acetone–benzene solution the product melted at 39–41° and weighed 110 g. (60% yield). It was then further crystallized to a constant melting point of 42–43°.

Anal. Calcd. for C₄₈H₉₂O₄: C, 78.63; H, 12.64; iodine no., 34.7; sap. no., 153. Found: C, 78.87; H, 12.63; iodine no., 35.9; sap. no., 158.

Saponification of the diester was accomplished by refluxing with 0.5 N alcoholic potassium hydroxide for one hour. The product was separated into an alkali soluble and insoluble portion. The alkali insoluble product was crystallized six times from alcohol to a constant melting point of 62–63.5°. This product showed no depression in melting point when mixed with a sample of lauroin prepared from methyl laurate and sodium.⁵

The alkali soluble portion was acidified with hydrochloric acid and the product crystallized from acetone. It melted at 44–45° and showed no melting point depression with known lauric acid. The 2-alkylbenzimidazole⁶ melted at 107–107.5° and was not depressed in melting point when mixed with known 2-undecylbenzimidazole.

Preparation of the Dimyristate of 14-Octacosene-14,15-diol.—Sodium wire (13.8 g., 0.6 mole) in 500 cc. of dry ether was treated over a period of two and one-half hours

(1) Pearl, Evans and Dehn, *THIS JOURNAL*, **60**, 2478 (1938).(2) Münchmeyer, *Ber.*, **19**, 1846 (1886).(3) Klinger and Schmitz, *ibid.*, **24**, 1271 (1891).(4) Basse and Klinger, *ibid.*, **31**, 1217 (1898).(5) Hansley, *THIS JOURNAL*, **57**, 2303 (1935).(6) Pool, Harwood and Ralston, *ibid.*, **59**, 178 (1937).

with 123.3 g. (0.5 mole) of myristoyl chloride dissolved in 150 cc. of dry ether. The mixture was then refluxed with stirring for ten hours. A yield of 67.8 g. (64%) of product was obtained which melted at 53.5–54.5° after three crystallizations from a 3:1 acetone–benzene solution. After two more crystallizations the product had a constant melting point of 54–55°.

Anal. Calcd. for $C_{36}H_{108}O_4$: C, 79.55; H, 12.88; iodine no., 30.0; sap. no., 132. Found: C, 79.41; H, 12.57; iodine no., 30.9; sap. no., 138.

A sample of the diester was saponified and the myristoin crystallized from alcohol to a constant melting point of 71–72°. The myristic acid obtained melted at 53–54°. The 2-tridecylbenzimidazole was prepared, m. p. and mixed m. p. 105–105.5°.

Preparation of the Dipalmitate of 16-Dotriacontene-16,17-diol.—This was prepared similarly. The crude product weighed 83 g., and after three crystallizations from dry 3:1 acetone–benzene 61 g. (70% yield) of a product melting at 50–60° was obtained. It was crystallized four times from dry 3:1 acetone–benzene and twice from 1:1 ether–alcohol to a constant melting point of 61–62°.

Anal. Calcd. for $C_{64}H_{124}O_4$: C, 80.26; H, 13.05; iodine no., 26.6; sap. no., 117. Found: C, 80.31; H, 12.70; iodine no., 26.7; sap. no., 117.

Saponification of this product gave palmitoin, m. p. 74–75°, and palmitic acid, m. p. 62–63°. The 2-pentadecylbenzimidazole was prepared, m. p. and mixed m. p. 95–96°.

Preparation of the Distearate of 18-Hexatriacontene-18,19-diol.—This was prepared similarly. The crude product was obtained in 67% yield, 36.1 g., m. p. 61–67°. This was crystallized to a constant melting point of 67–68°.

Anal. Calcd. for $C_{72}H_{140}O_4$: C, 80.83; H, 13.19; iodine no., 23.7; sap. no., 105. Found: C, 80.31; H, 12.86; iodine no., 23.4; sap. no., 109.

Saponification of the diester gave stearoin, m. p. 83–84° (Hansley⁶ reported 82–83°), and stearic acid, m. p. 69–70°. The 2-heptadecylbenzimidazole had m. p. and mixed m. p. of 69–70°.

Summary

1. Lauroyl, myristoyl, palmitoyl and stearyl chlorides react with metallic sodium in anhydrous ether to give the respective diesters of the enediols.

2. A mechanism for the reaction has been proposed.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN]

Silica Gels from Various Acids. Effect of Concentration and Mixtures on Setting Time¹

BY HERBERT L. DAVIS AND KENNETH D. HAY

Many extensive investigations demonstrate that the time required for a mixture of sodium silicate and acid to set depends on the concentration of silica, the pH value, and the temperature.^{2,3} The purposes of the present work were: (a) to show a range of common acid concentrations over which gels setting in an hour or less might be obtained with a commercial sodium silicate yielding 3.7% silica in the final system, (b) to seek a demonstrable lyotropic effect of negative ion of the acid, and (c) to investigate the behavior of mixtures of two acids.

Preparation of the Gels

The sodium silicate employed for all tests was the Number 9 grade from du Pont, sold as having 8.9% sodium oxide and 29% silicon dioxide or a ratio of 1:3.25. The original material was diluted with two volumes of distilled water, giving a specific gravity of 1.162, and titration with

standard acid showed it to be 1.55 *N* alkali using phenolphthalein, and 1.70 *N* alkali, using methyl orange as indicator. Standard 4.0 *N* solutions of hydrochloric, sulfuric, phosphoric, and acetic acids were prepared using phenolphthalein, so that phosphoric acid was treated as a dibasic acid. Especially in the rapidly setting gels the order of mixing is significant, so that for all tests here reported 40 ml. of acid was poured into 25 ml. of the silicate solution in a 100-ml. beaker at room temperature (25°), and the solutions mixed by pouring back and forth several times. Rapid mixing of the well-agitated solutions prevented local precipitation, and the mixtures remained fairly clear until the time for setting approached. The gel was considered set when a 7-mm. glass rod 9 cm. long, inserted in the mixture to the bottom of the beaker at about 20° from the vertical just failed to fall.² The setting seems to be preceded by the formation of a relatively tough surface film which must be broken. Too many tests in one place do interfere with the final set so that new areas of the gel must be chosen. Observation of these precautions resulted in good check determinations for most of the systems reported.

The 4 *N* acids were diluted to 1.0 and 2.0 *N* by means of calibrated burets, and the proper volumes of these acids taken so that dilution to 40 ml. gave the desired normality. For the strongly acid systems, appropriate volumes of the standardized c. p. concentrated acids were diluted to 40

(1) Read at the Milwaukee meeting of the American Chemical Society, September, 1938.

(2) C. B. Hurd, *J. Chem. Ed.*, **14**, 84 (1937).

(3) H. B. Weiser, "Inorganic Colloid Chemistry," Vol. II, "The Hydrous Oxides and Hydroxides," John Wiley and Sons, Inc., New York, 1935, p. 194.