pressure were taken in a Cottrell apparatus specially designed for a small quantity of liquid, about 2 cc. The vertical portion of this had a sealed on vacuum jacket surrounding the Anschütz thermometer.

For taking a melting point, a portion of the liquid sufficient to cover the bulb of the thermometer was put in a test-tube. By alternately freezing and melting the melting temperature was obtained. Then the same amount of a substance of known melting point near that determined, was frozen and melted under the same conditions to calibrate the thermometer in that particular region.

Summary

The α,ω-dimercaptans up to dodecamethylene have been prepared. Their properties have been determined and compared with those of the corresponding glycols and dibromide.

BALTIMORE, MD. RECEIVED MAY 29, 1943

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Preparation of Nonane and Decane α,ω-Dicarboxylic Acids[1]

BY WILLIAM P. HALL[2] AND E. EMMET REID

These acids, though known for a long time, have not been readily available. We have found that a mixture of the two is easily obtained by the nitric acid oxidation of μ-hydroxystearic acid from hydrogenated castor oil. According to whether the chain breaks at the one side or at the other of the hydroxyl group, heptoic acid and a C_{11} dibasic acid or hexoic and a C_{12} dibasic acid are obtained. Actually all four of these acids and some sebacic are produced. The monobasic acids are largely eliminated by steam distillation and the remaining mixture of acids is converted into the ethyl esters which are then separated by fractionation. The 175–178° and the 184–186° fractions at 8 mm. of the esters were 20 and 13%, respectively, of the weight of the starting material, or about 40% of the calculated which is satisfactory considering the low cost of the starting materials. That they were the desired materials was shown by their saponification numbers. The fact that the properties, particularly the melting points, of the glycols, dibromides and dimercaptans made from them fit into the respective series is even more convincing. The yields might well be pushed higher by further experimentation but our aim was to find a practicable method of preparation of the esters from which the acids may be obtained by saponification. Asalima and Takimoto[3] oxidized five grams of hydroxystearic acid and obtained a solid acid of average mol. wt. 221, which is between 216 and 230, the molecular weights of the C_{11} and C_{12} dibasic acids. We found fractionation of the esters of suberic and azelaic acids obtained by the oxidation of ricinoleic acids according to Vogel[4] and Baker and Ingold[5] to be a satisfactory method of separation of the esters of these acids.

Experimental

The oxidation was carried on in a 12-liter balloon flask fitted with an efficient mechanical stirrer. To 4 liters of concd. nitric acid, containing 1 g. of ammonium vanadate and heated nearly to boiling, 1 kilo of the hydroxystearic acid was added in small portions at such a rate that the reaction could be kept under control. After this addition the stirring and heating were continued until the heavy fumes died down, which took about eight hours. The slow evolution of red fumes never ceased. The mixture was steam distilled to remove the most of the monobasic acids. The mass was then cooled and the solid acid filtered off and washed on the filter. The air-dry weight of the dibasic acids was always high owing to retained monobasic acids and unoxidized starting material. The solid dibasic acid mixture was esterified and the purified ethyl esters fractionated at 8 mm., taking cuts at 175–178° and 184–186° which corresponded to plateaus in the distillation curve. These boiled at 120–122° and 130–132° at 0.5 mm. and gave saponification numbers of 408.9 and 389.9 compared with the calculated 412.0 and 391.8 of the desired esters.

Summary

Nitric acid oxidation of μ-hydroxystearic acid gives a mixture of mono- and di-basic acids. From this by esterification and fractionation the ethyl esters of the C_{11} and C_{12} dibasic acids may be obtained in satisfactory yields.

BALTIMORE, MD. RECEIVED MAY 29, 1943

---

[1] Original manuscript received July 25, 1941.

[2] From part of dissertation, Johns Hopkins University, 1936.

[3] Asahina and Takimoto, *J. Pharm. Soc. Japan*, **49**, 1017 (1929); *C. A.*, **24**, 1346 (1930).

[4] Vogel, *J. Chem. Soc.*, **123**, 2023 (1923).

[5] Baker and Ingold, *ibid.*, **123**, 122 (1923).