SHORT COMMUNICATIONS

The Oxidation of 9:10 Diketostearic Acid by Peracetic Acid (Baeyer and Villiger Reaction)

ABSTRACT

Diketostearic acid 9:10 is readily and speedily oxidized by peracetic acid, at low temperatures to high yields of azaleic acid and nonanoic acids.

Diketostearic acid 9:10 (Stearoxylic acid) was prepared from stearolic acid by the method of Khan and Newman (1). Stearolic acid, 5.6 g, (prepared from oleic acid by bromination at 0 C in petrol ether solution followed by dehydrobomination with methanolic potassium hydroxide) was dissolved in a solution of 1.5 g KOH in 100 cc water and diluted to 3 liters. Sodium bicarbonate, 1 g, was added and the pH adjusted to ca. 7.5 by the passage of CO_2 gas until the mixture was only very faintly pink to phenolphthalein. A solution of 6.3 g potassium permanganate in 300 cc water was added all at once and the mixture was maintained at 25 C for 60 min. Then the excess permanganate was removed by passage of SO_2 gas until colorless. The product was filtered off, washed with water and recrystallized from 80 cc of 95% ethanol. Pale lemon crystals were obtained, mp = 84-85 C, neutralizing equivalent = 310. (Diketostearic acid requires mp = 85 C, neutralizing equivalent = 312.)

Oxidation of Diketostearic Acid With Peracetic Acid

Diketostearic acid (3.12 g, 0.01 mole) was dissolved in 40 cc glacial acetic acid by warming gently to ca. 40 C. Then 10 cc 30% hydrogen peroxide (100 vol) was added. This caused the precipitation of the diketo-acid, giving the mixture the consistency of a thick slurry. After 5 min the mixture became clear and homogeneous, and after a further 20 min the last traces of the yellow color due to the diketo-acid had disappeared. The reaction was evidently more or less complete, but the mixture was allowed to stand for a further 18 hr at 28 C. It was then diluted with 300 cc^3 water and extracted three times with petroleum ether (3 x 100 cc^3) to remove the monobasic acid scission product. On removal of the solvent, 1.502 g of product was obtained, mp = 12.5 C., neutralizing equivalent = 160, n_D^{20} = 1.4310. (Nonanoic acid requires mp = 12.5 C, neutralizing equivalent = 158, n_D^{20} = 1.43057.) Yield was 95.05%.

The extracted aqueous solution was further extracted with four successive quantities of ether. On removal of the solvent, 1.740 g residue was obtained. This was recrystallized from water, when the final product had mp = 106.5 C, neutralizing equivalent = 94. This corresponds to azaleic acid. Yield was 92.55%.

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REFERENCE

1. Khan, N.A., and M.S. Newman, J. Am. Chem. Soc. 1952:1063.

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Rapid Methods for Determination of Free Fatty Acids Contents in Fatty Oils

ABSTRACT

Rapid qualitative and quantitative methods for determining the free fatty acid (FFA) contents in common oils and fats are reported. Qualitative method is based on the type of color developed in the presence of BDH indicators (Universal and "678") when a known excess of alkali is added to an alcoholic solution of oil or fat. By this method, low (0.0-0.25), medium (0.26-0.99) and high (1.0 and above) FFA levels in fatty oils may be distinguished. Quantitative method is a simplified modification of the usual procedure of determining the FFA contents of oils and fats by titration against standard alkali solution in the presence of BDH Universal or "678" indicator. The results of the rapid methods agree well with those of the standard AOCS method.

TABLE I

Colors and Free Fatty Acid (FFA) Contents

Range	FFA level	Color developed
With BDH Universal indicator		
Low	0.0-0.25	Indigo to blue
Medium	0.26-0.99	Green to yellowish green
High	Over 1.0	Yellow, orange, buff or chocolate
With BDH "678" indicator		
Low	0.0-0.25	Violet or indigo
Medium	0.26-0.99	Light blue to light green
High	Over 1.0	Yellow to orange yellow

Fatty oils may contain low or high FFA. Raw oils might look like alkali-refined oils. Tests have been developed to rapidly (a) distinguish between low and high FFA content oils and (b) determine the FFA contents in such oils.