A Note on the Preparation of Alkyl Linolenates

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ROLLET'S (1) procedure for the preparation of the esters of linolenic acid by the removal of the bromine from hexabromostearic acid with zinc in boiling alcohol requires the addition to the reaction mixture in the course of one hour of approximately fifteen equivalents of 7.5 N absolute alcoholic HCl per mol of hexabromide. The acid markedly accelerates the debromination, which is considered complete when the reaction mixture becomes clear, a subsequent refluxing for three or four hours insuring complete esterification. However, the preparation of anhydrous alcoholic HCl is very troublesome, and equivalent solutions of alcoholic H_2SO_4 are usually substituted whenever possible. Thus, the latter acid is perfectly suitable for the debromination of tetrabromostearic acid, which reacts violently with zinc in warm alcohol even in the absence of inorganic acids. The only apparent function of the added acid in this case is to promote the esterification of the resulting linoleic acid.

On the other hand, we have observed that the debromination of the less reactive hexabromostearic acid is actually hindered by 7.5 N alcoholic H_2SO_4. In attempting to prepare ethyl and methyl linolenates using this solution, we found that even with large excesses of the absolute alcohols and refluxing for periods up to 10 hours, no clarification of the reaction mixture occurred and much of the hexabromide could be recovered unchanged or partly esterified. When the acid solution was added very slowly over a period of two hours after a preliminary boiling of the zinc and hexabromide mixture in neutral alcohol, good yields of linolenates were usually obtained, since the debromination could then take place before the accumulation of sufficient interfering material.

These results may be readily accounted for by the extremely low solubility of $ZnSO_4$ in absolute alcohols, the salt undoubtedly forming a protective coating over the unreacted zinc and hexabromostearic acid and thereby hindering the reaction. Furthermore, where debromination is successfully accomplished under the conditions mentioned above, the suspended salt makes it difficult to recognize the completion of the reaction and it also complicates the extraction of the linolenic esters from the acid alcohol unless it is first dissolved by the addition of much water, a step which should be avoided where a colorless product of low acid value is desired. Kimura (2) has shown that the reduction of hexabromostearic acid proceeds smoothly with zinc dust and approximately 18.7 N alcoholic H_2SO_4, but such a concentration of sulfuric acid may be considered undesirable in a mixture with the very sensitive unsaturated esters. We, therefore, prefer to follow Rollet's original procedure and use finely divided zinc to accelerate the reaction, since the hexabromostearic acid reacts rather sluggishly with the coarser metal. When equal weights of zinc dust and finely powdered hexabromide suspended in 2½ parts of boiling alcohol are treated dropwise and under reflux with 2½ parts of approximately 7.5 N alcoholic HCl, the reaction mixture becomes clear within 10 minutes after the addition of the acid is begun. The rapid debromination and subsequent ease of extraction of a colorless ester with a practically theoretical iodine number amply compensate for the inconvenience of preparing the anhydrous alcoholic HCl.

BIBLIOGRAPHY

1. Rollet, A., Z. physiol. Chem., *62*, 422 (1909).
2. Kimura, W., Fettchem. Umschau, *42*, 78 (1935).

Report of the Committee on Soap In Refined Oil-1939-40

DURING the past year the committee has been testing the Modified Durst-Stillman Method as published in the Committee Report, 1939 (OIL & SOAP, *16*, 133). In addition, the method was tested in two laboratories that had not previously used the procedure.

Our work indicates:

(1) In the hands of an experienced analyst, the method, as reported, is the most satisfactory method, both from the standpoint of accuracy and time required that we have tested.

(2) The method usually gives high results when the amount of soap present is 25 parts per million or less. The reason for this is not clear. The end point, however, is only accurate to about 10 parts per million and this would account for most of the difficulty at low soap concentration.

(3) Analysts trying the procedure for the first time invariably get high results. This is undoubtedly due to incomplete baking out of hydrochloric acid.

We intend next year to study the method at soap concentrations under 50 parts per million and to work out a test for incomplete removal of hydrochloric acid.

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