Preparation of Long-Chain Fatty Acid Chlorides[1, 2]

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THE ACYL CHLORIDES of the long-chain fatty acids are widely used in the synthesis of glycerides and other derivatives. The usual procedure for their preparation is to react the acid with a chlorinating agent, such as phosphorus pentachloride, phosphorus trichloride, thionyl chloride, or oxallyl chloride, and separate the acid chloride from the reaction mixture by vacuum distillation. Bauer (1) investigated the yields of saturated and unsaturated acid chlorides, using the various chlorinating agents with and without solvents. Yields of the distilled product varied from 19.2 to 98.8%. Craig *et al.* (2) obtained better yields for oleoyl, stearoyl, and palmitoyl chlorides by following the procedure outlined by Bauer but with an improved vacuum-distillation technique, which avoided decomposition and polymerization.

Ralston *et al.* (3), in a patent assigned to Armour and Company, claimed that, in experiments using phosphorus pentachloride and trichloride, the excess chlorinating agent and the reaction by-products could be removed by washing the reaction mixture with water without substantial hydrolysis of the acid chlorides. It has been found that excellent results are obtained if the chlorination and subsequent water-washings are carried out in an organic solvent. The use of an inert solvent with a low water-solubility reduces hydrolysis of the acid chlorides and facilitates removal of the reaction by-products. The material remaining in the solvent is essentially the acid chloride, which contains only a small amount of free acid. The product is recovered simply by evaporating the solvent, thus avoiding vacuum distillation.

Experimental

The initial work was carried out on oleic acid, using phosphorus pentachloride and Skellysolve "F" (a petroleum solvent with a boiling range of 35 to 58°C.). Ten g. (0.035 moles) of oleic acid (I. V. 89.6) were dissolved in 100 ml. of Skellysolve "F," and 7.5 g. (0.036 moles) of phosphorus pentachloride were added to the solution. The mixture was refluxed for 1 hr. The solution was cooled to room temperature and washed twice with ice water. Excessive shaking was avoided, and the water layer was drawn off as soon as it separated to minimize hydrolysis of the oleoyl chloride. The organic phase was dried with anhydrous sodium sulphate, and the solvent was removed under vacuum to give a quantitative recovery of a product with an iodine value of 84.4 (theoretical 84.6). A colorimeteric test for phosphorus, using perchloric acid and molybdate reagent (4), showed only a trace amount. The oleic acid remaining in the product was determined by infrared analysis. A Perkin-Elmer, Model 21, infrared spectrophotometer was used. The samples were analyzed as carbon tetrachloride solutions (15–30%) in a 0.11-mm. sodium chloride absorption cell. As shown in Figure 1, the carbonyl of the free acid absorbs at 1,700 cm^{-1} whereas that of the acid chloride absorbs at 1,800 cm^{-1}. The optical density of the free acid at 1,700 cm^{-1} was found to obey Beer's law over the concentration range involved (Figure 2) so that the percentage of acid in the acid chloride can be calculated directly from the optical density at 1,700 cm^{-1}. For the sample of oleoyl chloride prepared above, the spectra of which is shown in Figure 1, the concentration of oleic acid was calculated to be 1.2%.

Similar results were obtained with stearic acid and tetrabromostearic acid, *i.e.*, quantitative recovery of

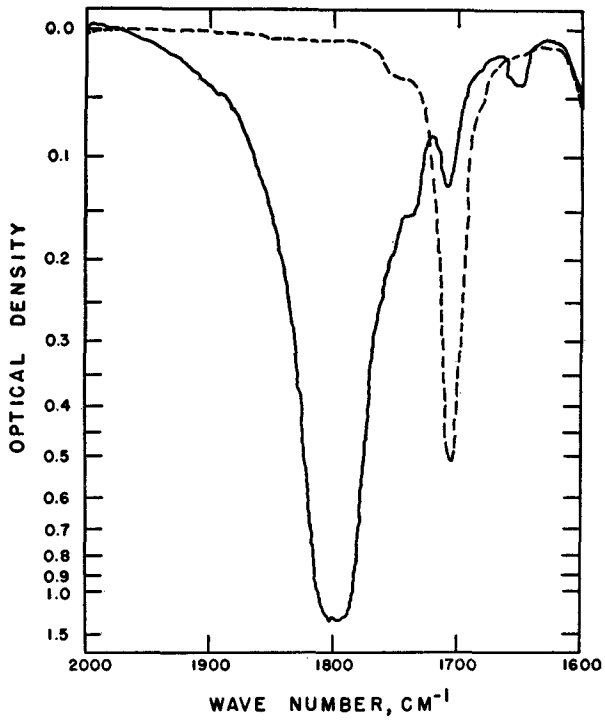

FIG. 1. Infrared absorption spectra.
– – – – – oleic acid
——— oleoyl chloride

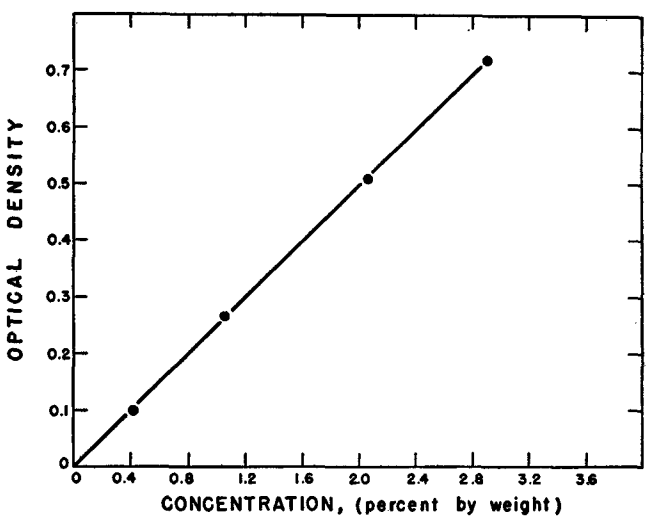

FIG. 2. Optical density at 1,700 cm^{-1} *vs.* concentration of oleic acid.

[1] Presented at the fall meeting, American Oil Chemists' Society, Philadelphia, Pa., Oct. 10–12, 1955.
[2] Issued as N. R. C. No. 4240.

TABLE I
Conversion of Commercial Stearic Acid to the Acid Chloride

Chlorinating agent	Solvent	% Free acid in product
PCl_5	Skellysolve F	1.7
PCl_5	Benzene	1.4
PCl_5	Carbon tetrachloride	0.7
PCl_3	Skellysolve F	4.8
PCl_3	Benzene	0.8
PCl_3	Carbon tetrachloride	1.1

the product containing less than 1.5% free acid based on infrared analysis. In the case of tetrabromostearic acid 4.0 g. of phosphorus pentachloride was used with 10 g. of acid, and the solution was washed with water at room temperature to avoid crystallization of the tetrabromo-stearoyl chloride.

Since the method could be readily adapted to the commercial preparation of the acid chlorides, a number of runs was also made, using a sample of commercial stearic acid [3] with both phosphorus pentachloride and trichloride in three different solvents. Ten g. of acid were placed in 100 ml. of solvent, and 7.5 g. of the pentachloride or 5.0 g. of the trichloride were added, and the mixture was refluxed for 1 hr. The results of these runs are given in Table I. A layer of phosphoric acid formed on the sides of the reaction flask with the trichloride, and there was a slight absorption at 1,740 cm^{-1} in the infrared spectra, which was believed to be caused by a small amount of anhydride formation.

[3] Obtained from W. C. Hardesty Company of Canada Limited.

Summary

A rapid method has been found for preparing the long-chain fatty acid chlorides, which eliminates purification by distillation. It gave a quantitative yield of product containing less than 1.5% free acid. The method involves treating the free acid with phosphorus pentachloride or trichloride in an inert organic solvent and removing the excess chlorinating agent by washing the solvent phase with water. Phosphorus pentachloride and Skellysolve "F" were preferred for laboratory preparations. For commercial purposes however either chlorinating agent could be used in a variety of inert organic solvents.

Infrared analysis was found to give a rapid measure of the free acid content of the prepared acid chlorides.

REFERENCES

1. Bauer, S. T., Oil and Soap, *23*, 1 (1946).
2. Craig, B. M., Lundberg, W. O., and Geddes, W. F., J. Am. Oil Chem. Soc., *29*, 169 (1952).
3. Ralston, A. W., McCorkle, M. R., and Vander Wal, R. J., U. S. Patent 2,262,431.
4. King, E. J., Biochem. J., *26*, 292 (1932).

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The Work of the Technical Safety Committee

A. ERNEST MacGEE, Skelly Oil Company, Kansas City, Missouri

Minutes of the Technical Safety Committee Meeting, September 25, 1956

A. Ernest MacGee, chairman, welcomed to the meeting T. H. Hopper, president of the Society, and Howard Black, vice president. Both expressed pleasure at seeing the safety work successfully getting under way and commended those present, particularly the members of the Technical Safety Committee, for their participation for the general good of the cause. MacGee then pointed out that this meeting would serve the two-fold purpose of conducting a safety symposium of formal papers and effecting a meeting for the purpose of conducting current business of the committee. The group attending the session was composed of 15 members of the committee and about 70 other members of the Society interested in the session's activities. Committee members were:

Rex Wingard, Blaw-Knox Company, Chicago, Ill.
Fred K. Bieri for R. W. Cornell, Pittsburgh Plate Glass, Red Wing, Minn.
Walter F. Bollens, Swift and Company, Chicago, Ill.
Wm. T. Coleman, Western Cottonoil Company, Abilene, Tex.
H. D. Fincher, Anderson, Clayton and Company, Houston, Tex.
Ralph P. Hutchins, French Oil Mill Machinery Company, Piqua, O.
George J. Hutzler, Spencer Kellogg and Sons, Buffalo, N. Y.
Henry James, Ralston-Purina Company, St. Louis, Mo.
A. Ernest MacGee, Skelly Oil Company, Kansas City, Mo.
Paul R. Sheffer, Corn Products Refining Company, Argo, Ill.
Louis M. Smith, A. E. Staley Mfg. Company, Decatur, Ill.
Norman H. Witte, Central Soya Company, Inc., Decatur, Ind.
Harvey E. Marxhausen, Cargill Inc., Minneapolis, Minn.
W. J. Miller for Robert Stokes, Buckeye Cellulose, Cincinnati, O.
Don F. Starr for J. W. Dunning, V. D. Anderson Company, Cleveland, O.

Those indicated below, although unable to attend, took the time to write the chairman, explaining why and offering a number of suggestions in connection with the committee's work. Portions of these letters were read to the group by MacGee.

Robert Stokes, Buckeye Cellulose, Cincinnati, O.
John W. Dunning, The V. D. Anderson Company, Cleveland, O.
James H. Brawner, Southern Cotton Oil Company, New Orleans, La.
Reider Arneson, Archer-Daniels-Midland Company, Minneapolis, Minn.
Odell J. Jones, Western Cottonoil Company, Abilene, Tex.
F. P. Parkin, Borden's Soy Processing, Waterloo, Ia.
Reuben W. Cornell, Pittsburgh Plate Glass, Red Wing, Minn.
James K. Sikes, Plains Cooperative Oil Mill, Lubbock, Tex.

MacGee discussed the fact that safety permeated not only solvent-extraction plant activities but also extended throughout all plant manufacturing operations. In many of these safety matters there are things which are dependent upon scientific or technical features of both a fire hazard and health hazard nature, namely, things which properly, and in many cases with advantage, could be included in any broad activity of a technical safety committee. Although a number of things in this connection are generally accepted by all, many safety measures and practices are somewhat controversial and obviously can best be resolved by turning upon them the spotlight of knowledge of those chemists and engineers in the oil and fat industry whose daily work brings them into