



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

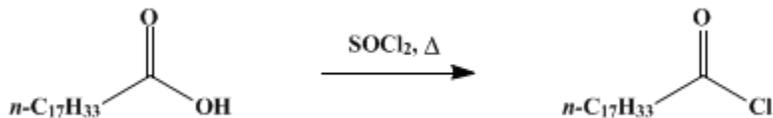
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.739 (1963); Vol. 37, p.66 (1957).*

## OLEOYL CHLORIDE



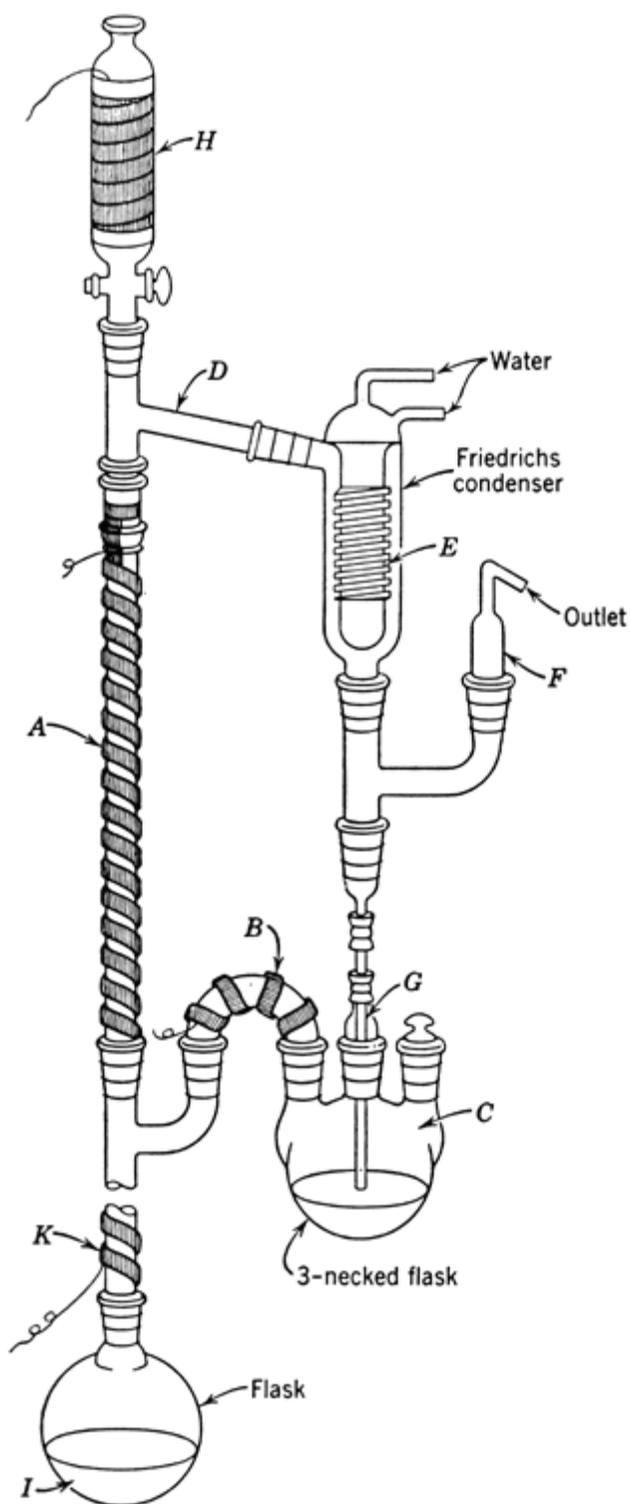
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Checked by Max Tishler and R. Connell.

### 1. Procedure

Seventy grams (0.25 mole) of **oleic acid** (**Note 1**) is placed in the dropping funnel *H* of the tangential apparatus (**Fig. 13**; **Note 2**). The **thionyl chloride** distillation is started and regulated (**Note 2**); the upper part of the column should be filled with the vapor, and reflux should be constant and steady. The acid is dropped in at the top of the column over a period of 35 minutes (120 g. per hour). The product that collects in the receiver *I* contains about 25–27% of **thionyl chloride** (**Note 2**) if the heated lower leg *K* is employed. The product in receiver *I* is heated on a steam bath under reduced pressure until the more volatile components are completely removed. The residue of crude acid chloride weighs 72–74 g. (97–99% yield). The infrared spectrum of this product shows no trace of a carboxyl band (**Note 1**), (**Note 3**), and (**Note 4**).

**Fig. 13.**



The crude acid chloride will serve for most purposes. It can be distilled at very low pressures (b.p. 99–109°/25  $\mu$ ) to yield a water-white product;  $n_D^{25}$  1.4580–1.4613 (Note 5). Small amounts of oleoyl chloride may be distilled at higher pressures; b.p. 180–185°/1–2 mm. The infrared absorption curve of the oleic acid obtainable by hydrolysis is the same as that of the oleic acid used; thus no isomerization during the reaction is indicated.

## 2. Notes

1. The **oleic acid** used by the submitters had a freezing point of  $-2^{\circ}$  to  $+13^{\circ}$  and a boiling point of  $182-187^{\circ}/1-2$  mm. It was a 90% middle cut from Emerson 233 as obtained from Emery Industries, Inc., Cincinnati, Ohio. The checkers found that the amount of color in the product was a function of the purity of the **oleic acid**. The product from distilled Emerson 233 was dark red-brown, whereas that from a purified grade of **oleic acid** was pale yellow.

2. The tangential apparatus<sup>2</sup> is built from stock pieces of glassware having 24/40 standard taper glass joints, and it is clamped to two ring stands. The reactor consists of a column 50 cm. long and 2 cm. inside diameter, packed with 1/8-in. glass helices of the type used for packing distillation columns, and wrapped with a 275-watt flexible heating tape *A*, 6 ft. long and 1/2 in. wide, with lead wires connected to a variable transformer such as the Powerstat or Variac, which is attached to a source of 110-volt power. Near the bottom of the column is a heated side arm connection *B* to a three-necked flask reservoir *C*. The use of the leg *K*, wrapped with a heating tape, removes much of the excess of **thionyl chloride** and is particularly advantageous with acid chlorides (such as **oleoyl chloride**) that are sensitive to heat. The crude effluent from the reactor ordinarily contains 40–50% of **thionyl chloride**, which is reduced one-half or more by this leg. It is not essential for use with chlorides insensitive to heat. Vapor supplied by boiling the liquid in the reservoir is forced to circulate via *B* through the column by sufficient heat input to the column and the lower leg *K*; the excess escapes at the top through the side arm *D* which is connected to a Friedrichs condenser *E*. The bottom of the condenser is connected to a Y-shaped section with an outlet *F* for effluent gas and a return *G* which extends below the surface of the liquid in the reservoir. At the top of the column is a 250-ml. dropping funnel *H* for admitting reactants to the column. Since **oleic acid** is a liquid at room temperature, heating of this funnel is not required in the present preparation. At the bottom of the column is a 500-ml. flask *I* for receiving the product.

3. Other acid chlorides can be prepared similarly. (a) **Palmitoyl chloride**: **Palmitic acid** is a solid at room temperatures (m.p.  $61-62^{\circ}$ ) and is not sufficiently soluble in **palmitoyl chloride** or **thionyl chloride**, and so these cannot be used as solvents. It is admitted to the reactor in the melted condition by warming the acid in the dropping funnel *H*. The quality of the chloride naturally depends on the homogeneity of the starting acid; **palmitic acid** usually contains a little **stearic acid**, which does not affect the melting point. **Palmitoyl chloride**,  $n_D^{25}$  1.4489, can be obtained as a water-white product by distillation at very low pressures (b.p.  $110^{\circ}/15-24$   $\mu$ ), or with negligible decomposition at boiling points as high as  $165^{\circ}$ .

(b) **Ricinoleoyl chloride**: b.p.  $205-210^{\circ}/8$  mm.,  $125-130^{\circ}/25$   $\mu$ ;  $n_D^{25}$  1.4759; this substance decomposes significantly at the higher distillation temperature.

(c) **2,4-Di-*tert*-amylphenoxyacetyl chloride**: In this instance, the corresponding solid acid (20 g.) is dissolved in the acid chloride (80 g.) as a solvent and admitted at the rate of 70 g. of acid per hour. The crude acid chloride, after removal of the excess **thionyl chloride**, contains about 1% of unchanged acid (infrared determination). The yield of distilled acid chloride, b.p.  $143-146^{\circ}/2$  mm.,  $n_D^{25}$  1.5062, is 85%.

4. The described procedure is not suitable for all acids. For instance, the acid chloride must not have a boiling point so near that of **thionyl chloride** that they are inseparable by distillation. Certain high-molecular-weight acids give dehydration products, presumably diketenes: e.g., behenic and dihydroxystearic acids.

5. The refractive index will vary with the purity of the **oleic acid**. **Oleic acid** purified by low-temperature crystallization and by conversion to the oleic acid-urea complex (95.3% oleic, 0.7% linoleic) yielded a product with  $n_D^{25}$  1.4613.

### 3. Discussion

This modification of the continuous reactor (cf. **benzoylacetanilide**, p. 80) with countercurrent distillation is preferred for reactions in which a large amount of solvent or excess of one reactant is essential, but increase of total volume is undesirable. It is especially useful if the substances involved are heat-sensitive; with this apparatus the reactants are heated for only a few minutes at most. It is particularly applicable to the preparation of acid chlorides from carboxylic acids and **thionyl chloride** (cf. (Note 3) and (Note 4)). An indefinite amount of product can be prepared by replenishing the reactants as they are consumed.

**Oleoyl chloride** has been prepared by treatment of **oleic acid** with **thionyl chloride**,<sup>3</sup> phosphorus trichloride or pentachloride, and **oxalyl chloride**.<sup>4</sup> The highest yield (86%) reported was secured by use of **oxalyl chloride** in **carbon tetrachloride**, but the more economical **phosphorus trichloride** gave a yield

of 60%. The standard procedures for obtaining aliphatic acid chlorides have been described many times without inclusion of details other than physical properties. Only references to the procedures useful in the laboratory are given.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 80](#)

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## References and Notes

1. Eastman Kodak Company, Rochester, New York.
  2. Allen, Byers, Humphlett, and Reynolds, *J. Chem. Educ.*, **32**, 394 (1955).
  3. Verkade, *Rec. trav. chim.*, **62**, 393 (1943); Fierz-David and Kuster, *Helv. Chim. Acta*, **22**, 82 (1939).
  4. Bauer, *Oil & Soap*, **23**, 1 (1946).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

oleic acid-urea complex

phosphorus trichloride or pentachloride

[thionyl chloride \(7719-09-7\)](#)

[carbon tetrachloride \(56-23-5\)](#)

[phosphorus trichloride \(7719-12-2\)](#)

[oleic acid \(112-80-1\)](#)

[palmitic acid \(57-10-3\)](#)

[stearic acid \(57-11-4\)](#)

[oxalyl chloride \(79-37-8\)](#)

[Benzoylacetanilide \(85-99-4\)](#)

[Oleoyl chloride \(112-77-6\)](#)

[Palmitoyl chloride \(112-67-4\)](#)

[Ricinoleoyl chloride](#)

[2,4-Di-tert-amylphenoxyacetyl chloride \(88-34-6\)](#)