



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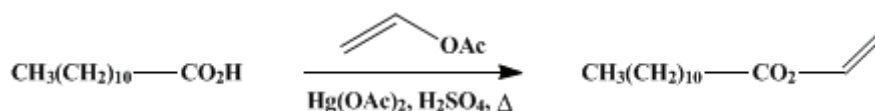
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.977 (1963); Vol. 30, p.106 (1950).

VINYL LAURATE AND OTHER VINYL ESTERS

[Lauric acid, vinyl ester]



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1. Procedure

In a 500-ml. round-bottomed three-necked flask provided with a thermometer, a reflux condenser, and a gas inlet tube through which a stream of nitrogen is passed (Note 1) are placed 206 g. (2.4 moles) of freshly distilled vinyl acetate (Note 2) and 80 g. (0.4 mole) of lauric acid (Note 3). The lauric acid is dissolved by warming, and 1.6 g. of mercuric acetate is added. The mixture is shaken by hand for about 30 minutes, and 0.15 ml. of 100% sulfuric acid is added dropwise (Note 4). The solution is heated under reflux for 3 hours, then 0.83 g. of sodium acetate trihydrate is added to neutralize the sulfuric acid. The excess vinyl acetate is recovered by distillation at atmospheric pressure (vapor temperature about 70–80°) until the pot temperature reaches 125° (Note 5). The distillation is completed at 10 mm. or lower (Note 5), and, after the collection of a small quantity of low-boiling material, fairly pure vinyl laurate (Note 6) is obtained as a colorless liquid, b.p. 142–143°/10 mm. (138–139°/8 mm.; 124–126°/3 mm.). The yield is 50–57 g. (55–63%). Redistillation (Note 7) yields 48–53 g. (53–59%) of pure vinyl laurate, b.p. 142–142.5°/10 mm. (120–120.5°/2 mm.); n_D^{25} 1.4387 (Note 8) and (Note 9).

2. Notes

- All operations should be conducted in a nitrogen atmosphere to minimize the formation of polymer.
- An Eastman Kodak Company practical grade of vinyl acetate is satisfactory. It was distilled immediately before use through a 48 by $\frac{3}{4}$ in. column packed with 3/32-in. single-turn Pyrex glass helices. The checkers employed material obtained from the Niacet Chemicals Division, Niagara Falls, New York, distilled once through a 12-in. Vigreux column, b.p. 73°/746 mm.
- Lauric acid, m.p. 44°, was prepared from the commercial acid obtained from Armour and Company, Chicago, Illinois. The acid was recrystallized twice from acetone at –40° (10 ml. of acetone per gram of acid) and distilled under reduced pressure through a well-insulated, electrically heated 30 by 1 in. column packed with $\frac{1}{4}$ -in. Berl saddles. Pure lauric acid has a boiling point of 167–168°/8 mm. and n_D^{45} 1.4316. The Eastman Kodak Company grade of lauric acid melting at 43–44° is satisfactory.
- The 100% sulfuric acid is prepared by cautiously adding 7.3 g. of fuming sulfuric acid containing 30% sulfur trioxide to 10 g. of 95% sulfuric acid.
- An electrically heated 18 by $\frac{1}{2}$ in. Vigreux column was employed.
- The vinyl laurate, which has an acid number of about 2, usually contains a small quantity of mercury at this stage, from which it can be separated by decantation.
- Sufficient sodium bicarbonate is added to the pot charge to neutralize the free acid present (Note 6).
- Additional properties of vinyl laurate are n_D^{35} 1.4345 and d_4^{30} 0.8639. If the iodine number is determined by the Wijs method, a 200% excess of iodine chloride solution and a 1-hour reaction period should be employed in order to obtain values which are 97–99% of the theoretical value.
- Vinyl caproate, caprylate, pelargonate, caprate, myristate, palmitate, stearate, 10-hendecenoate (undecylenate) and oleate can be prepared in a similar manner, except that in the preparation of the palmitate and stearate the fatty acids are added to a solution of mercuric acetate and sulfuric acid in vinyl acetate. Vinyl stearate is not redistilled, but the once-distilled product is recrystallized from acetone at 0° (3 ml. of acetone per gram of vinyl stearate). The amount of mercuric acetate employed was 2%, and the amount of 100% sulfuric acid was 0.3–0.4%, of the weight of the stearic acid. Average yields and properties of these vinyl esters are given in the table.

Vinyl Ester	Yield, %	Boiling Point °C. mm.		n_D^{30}	d_4^{30}
Caproate	40	98–99	100	1.4159	0.8837
Caprylate	55	134–135	100	1.4256	0.8719
Pelargonate	55	133–133.5	50	1.4291	0.8689
Caprate	45	148	50	1.4320	0.8670
Myristate	60	147–148	4.8	1.4407	0.8617
Palmitate (m.p. 26.7–27.1°)	35	168–169	4.5	1.4438	0.8602
Stearate (m.p. 35–36°)	30	187–188	4.3	1.4423 (at 40°)	0.8517 (at 40°)
10-Hendecenoate	70	124–124.5	10	1.4442	0.8799
Oleate	60	178	2.8	1.4533	0.8691

The acids used for preparing the vinyl esters tabulated were Eastman Kodak Company pure grade except for the following, which were obtained from the companies indicated and purified by fractionation through an efficient fractionating column: [caproic acid](#), b.p. 96°/8 mm., Carbide and Carbon Chemicals Corporation, New York; [caprylic acid](#), b.p. 124–125°/8 mm., [capric acid](#), b.p. 145–146°/8 mm., Armour and Company, Chicago, Illinois; [pelargonic acid](#), b.p. 176°/64 mm., Emery Industries, Cincinnati, Ohio; [10-hendecenoic \(undecylenic\) acid](#), b.p. 177–180°/25 mm., Baker Castor Oil Company, New York. [Oleic acid](#) was prepared from olive-oil fatty acids by low-temperature crystallization and distillation.²

3. Discussion

The procedure described is substantially that of Toussaint and MacDowell,³ with minor modifications.⁴ Vinyl esters of long-chain aliphatic acids have also been prepared by the reaction of [acetylene](#) with the appropriate acids,^{5,6,7,8} but this reaction is not so convenient for small-scale laboratory preparations.

The interchange reaction of [vinyl acetate](#) with [lauric acid](#) in the presence of [mercuric sulfate](#) has been studied,⁹ and [vinyl laurate](#) has been obtained also from [lauryl chloride](#) and [acetaldehyde](#) in the presence of [pyridine](#).¹⁰

References and Notes

1. Eastern Regional Research Laboratory, U. S. Department of Agriculture, Philadelphia, Pennsylvania.
2. Brown and Shinowara, *J. Am. Chem. Soc.*, **59**, 6 (1937); Wheeler and Riemenschneider, *Oil & Soap*, **16**, 207 (1939).
3. Toussaint and MacDowell, U. S. pat. 2,299,862 [*C. A.*, **37**, 1722 (1943)].
4. Swern, Billen, and Knight, *J. Am. Chem. Soc.*, **69**, 2439 (1947); Swern and Jordan, *J. Am. Chem. Soc.*, **70**, 2334 (1948); Asahara and Tomita, *Yushi Kagaku Kyōkaishi (J. Oil Chemists' Soc., Japan)*, **1**, 76 (1952) [*C. A.*, **47**, 3232 (1953)].
5. Reppe, Ger. pat. 588,352 [*C. A.*, **28**, 1357 (1934)]; U. S. pat. 2,066,075 [*C. A.*, **31**, 1037 (1937)]; Reppe et al., *Ann.*, **601**, 81 (1956).
6. Imperial Chemical Industries, Brit. pat. 581,501 [*C. A.*, **41**, 2428 (1947)].
7. Powers, *Ind. Eng. Chem.*, **38**, 837 (1946).
8. Otsuka, Matsumoto, and Murahashi, *Nippon Kagaku Zasshi*, **75**, 798 (1954) [*C. A.*, **51**, 13749 (1957)].
9. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).
10. Sladkov and Petrov, *Zhur. Obshchei Khim.*, **24**, 450 (1954) [*C. A.*, **49**, 6093 (1955)].

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

Vinyl caproate, caprylate, pelargonate, caprate, myristate, palmitate, stearate, 10-hendecenoate (undecylenate) and oleate

acetaldehyde (75-07-0)

sulfuric acid (7664-93-9)

acetylene (74-86-2)

sulfur trioxide (7446-11-9)

sodium bicarbonate (144-55-8)

nitrogen (7727-37-9)

mercuric acetate (1600-27-7)

mercury (7439-97-6)

iodine (7553-56-2)

acetone (67-64-1)

pyridine (110-86-1)

Caproic acid (142-62-1)

mercuric sulfate (7783-35-9)

oleic acid (112-80-1)

iodine chloride (7790-99-0)

caprylic acid (124-07-2)

stearic acid (57-11-4)

lauric acid (143-07-7)

Pelargonic acid (112-05-0)

vinyl acetate (108-05-4)

sodium acetate trihydrate (6131-90-4)

stearate

lauryl chloride (112-52-7)

10-hendecenoic acid (112-38-9)

Vinyl laurate,
Lauric acid, vinyl ester (2146-71-6)

palmitate

Vinyl stearate (111-63-7)

capric acid (334-48-5)

Vinyl Caproate

vinyl caprylate

vinyl pelargonate

vinyl caprate

vinyl myristate

vinyl palmitate

vinyl 10-hendecenoate

vinyl oleate