



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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

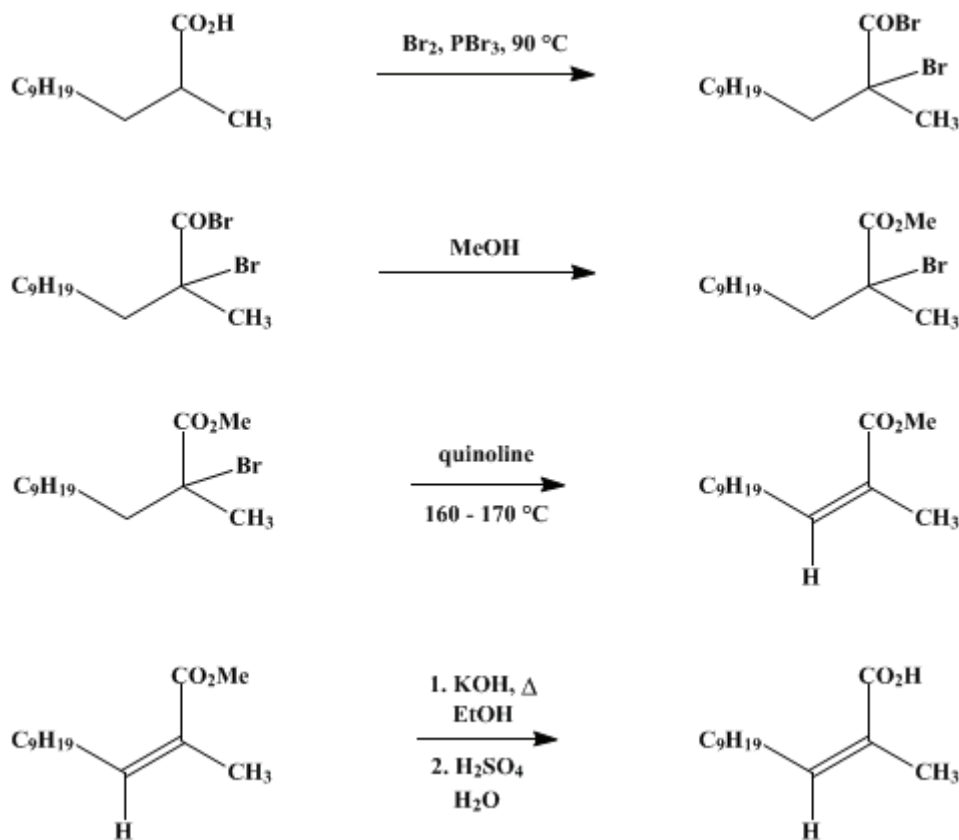
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.608 (1963); Vol. 38, p.43 (1958).*

## ***trans*-2-METHYL-2-DODECENOIC ACID**

[*trans*-2-Dodecenoic acid, 2-methyl-]



Submitted by C. Freeman Allen and Max J. Kalm<sup>1</sup>.

Checked by William S. Johnson and H. W. Whitlock, Jr..

### 1. Procedure

*Caution! The bromination and debromination steps should be carried out in a hood.*

Thirty grams (0.14 mole) of 2-methyldodecanoic acid is brominated exactly as described in the preparation of 2-methylenedodecanoic acid (p.616). The crude product, after the 18-hour heating period, is allowed to cool; then 56 ml. (1.4 moles) of commercial absolute methanol is added at such a rate that the exothermic reaction is kept under control (Note 1). The resultant pale-orange two-phase mixture is heated under reflux with stirring for 15 minutes, cooled, and diluted with 150 ml. of water containing about 2 g. of sodium sulfite. The bromo ester is extracted with two portions (75 ml. and 25 ml.) of petroleum ether (Note 2). The extracts are combined, washed with water, and dried over anhydrous sodium sulfate. The solvent is removed by flash distillation of the filtered solution from a 250-ml. flask heated on a steam bath, and the last traces of solvent are eliminated by reducing the pressure with a water aspirator. The crude bromo ester remaining amounts to 41.5–42.5 g. and is thermally unstable to distillation at reduced pressure.

The crude bromo ester is mixed with 82.5 ml. (0.70 mole) of pure quinoline (Note 3) in a 250-ml. round-bottomed flask equipped with an air condenser, and the mixture is heated for 3 hours with an oil bath maintained at 160–170°. The black mixture is cooled, treated with 150 ml. of 20% hydrochloric acid, then shaken thoroughly with 200 ml. of petroleum ether (Note 2) until most of the tarry material

has dissolved (Note 4). The aqueous phase is separated and washed with an additional 200 ml. of petroleum ether, and the combined organic extracts are washed with 10% hydrochloric acid and then with water. This washing cycle is repeated until the washes are colorless (two acid washes usually suffice); finally, the petroleum ether solution is washed once more with water. The organic layer is dried over anhydrous sodium sulfate, the solvent is flash-distilled as described above, and the residual liquid ester is distilled through a 61-cm. Podbielniak-type column (Note 5). The colorless unsaturated ester (Note 6) distils at 153–154°/14.5 mm. after a small fore-run. The yield is 22–27 g. (70–85.5% based on 2-methyldodecanoic acid),  $n_D^{25}$  1.4520–31,  $\lambda_{\max}$  214 m $\mu$ ,  $\epsilon$  12,300, in hexane (Note 7),  $\lambda_{\max}$  217 m $\mu$ ,  $\epsilon$  12,800, in 95% ethanol.

The ester is hydrolyzed by heating under reflux for 1.5 hours with 50 ml. of 95% ethanol and 4.4 g. of 85% potassium hydroxide (0.066 mole) for each 10 g. (0.044 mole) of ester. Two-thirds of the ethanol is removed by distillation; then the residue is diluted with five volumes of water and acidified to Congo red with 5N sulfuric acid. The organic acid is extracted with two 150-ml. portions of petroleum ether (Note 2), washed with water, and dried over anhydrous sodium sulfate. The petroleum ether is removed from the extracts by flash distillation as described above, and the residual acid is distilled at reduced pressure through a 61-cm. Podbielniak-type column (Note 5). The 2-methyl-2-dodecenoic acid, distilling at 166–168°/3 mm., is obtained in 68–83% over-all yield (20–24.5 g. from 22–27 g. of ester) (Note 8) and (Note 9), m.p. 28.5–32° to 29.5–32.4°,  $\lambda_{\max}$  218 m $\mu$ ,  $\epsilon$  12,900, in hexane (Note 7),  $\lambda_{\max}$  216–217 m $\mu$ ,  $\epsilon$  12,800, in 95% ethanol.

## 2. Notes

1. About 20 minutes is required. It may be desirable to cool the flask during the addition.
2. Commercial hexane, b.p. 65–68°, from petroleum fractionation is satisfactory.
3. Eastman Kodak Company white label grade synthetic quinoline was used. The use of coal tar quinoline introduces nonextractable aromatic impurities which contaminate the product.
4. The tarry material apparently consists of quinoline salts and some insoluble polymers.
5. A simplified Podbielniak column was employed.<sup>2</sup> Other columns of comparable efficiency should be suitable.
6. This methyl *trans*-2-methyl-2-dodecenoate is contaminated with 10–15% of methyl 2-methylenedodecanoate. Little, if any, *cis* isomer, which boils at the same temperature as the methylene isomer, is present. The methylene ester, which boils less than 10° below the desired isomer, can be separated by careful fractionation through an efficient column such as the 1.5-m. simple Podbielniak-type column.<sup>2</sup> The esters are more easily fractionated than are the higher-boiling acids. A significant fraction of the  $\alpha,\beta$ -unsaturated ester is transformed into an unidentified material of similar molecular weight when stored for several weeks in contact with air. The contaminant cannot be separated by ordinary distillation. The acid is much more stable to storage.
7. Optically pure hexane is preferred to ethanol as a solvent for absorption measurements below about 220 m $\mu$ . Commercial hexane from petroleum fractionation can usually be rendered optically pure by stirring overnight twice with 15% fuming sulfuric acid (1 lb. of the acid to about 3 l. of hexane), followed by a wash with 5% aqueous sodium hydroxide and distillation from sodium hydroxide pellets.
8. The carbon-carbon double bond is not isomerized to a detectable extent during saponification of the ester or distillation of the acid; thus the 2-methyl-2-dodecenoic acid will have the same isomeric composition as the sample of ester from which it was obtained, and it consists entirely of  $\alpha,\beta$ -unsaturated isomers.
9. *trans*-2-Methyl-2-dodecenoic acid, freed from isomeric impurities by fractionation through a 1.5-m. Podbielniak-type column, distilled at 146–147°/1.4 mm.,  $\lambda_{\max}$  217 m $\mu$ ,  $\epsilon$  14,500, in hexane. Since several consecutive fractions showed these properties, they are believed to represent the properties of the pure isomer. The quantity of such material recovered is entirely dependent on the efficiency of the column and the distillation procedure. Pure samples of solid acids may be readily secured by crystallization. Those prepared<sup>3</sup> by this procedure include: 2-methyl-2-eicosenoic acid, m.p. 66.3–67.6°,  $\lambda_{\max}$  217 m $\mu$ ,  $\epsilon$  13,490, in 54% yield; 2-methyl-2-hexacosenoic acid, m.p. 85.4–86.2°,  $\lambda_{\max}$  217 m $\mu$ ,  $\epsilon$  14,000, in 20% yield; 2,4-dimethyl-2-pentacosenoic acid, m.p. 69.5–70.3°,  $\lambda_{\max}$  218 m $\mu$ ,  $\epsilon$  14,550, in 19% yield. The lowered yields arise from difficulties in purification of the higher molecular weight isomers.

### 3. Discussion

2-Methyl-2-dodecenoic acid has been prepared by bromination of methyl 2-methyldodecanoate with N-bromosuccinimide, followed by dehydrobromination with quinoline and saponification of the ester.<sup>4</sup> The present procedure is an adaptation of the method of Cason, Allinger, and Williams.<sup>4</sup>

---

### References and Notes

1. University of California, Berkeley, California.
  2. Cason and Rapoport, *Laboratory Text in Organic Chemistry*, 2nd ed., p. 293, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962.
  3. Cason and Kalm, *J. Org. Chem.*, **19**, 1836 (1954).
  4. Cason, Allinger, and Williams, *J. Org. Chem.*, **18**, 842 (1953).
- 

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

petroleum ether

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

sodium sulfite (7757-83-7)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

potassium hydroxide (1310-58-3)

Quinoline (91-22-5)

N-bromosuccinimide (128-08-5)

hexane (110-54-3)

trans-2-Dodecenoic acid, 2-methyl-,  
trans-2-Methyl-2-dodecenoic acid (53663-29-9)

2-methyldodecanoic acid (2874-74-0)

2-Methylenedodecanoic acid (52756-21-5)

2-methyl-2-dodecenoic acid

methyl 2-methylenedodecanoate

2-methyl-2-eicosenoic acid

2-methyl-2-hexacosenoic acid

2,4-dimethyl-2-pentacosenoic acid

methyl 2-methyldodecanoate

methyl trans-2-methyl-2-dodecenoate