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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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.

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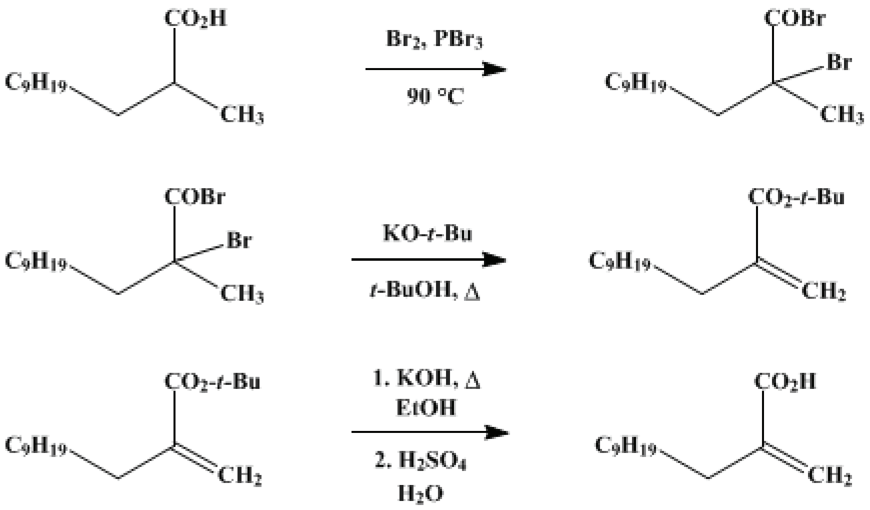
2-METHYLENEDODECANOIC ACID

[Dodecanoic acid, 2-methylene-]



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1. Procedure

Caution! The bromination step should be carried out in a hood, and appropriate precautions should be employed in handling potassium (Note 1).

A 250-ml. three-necked flask fitted (glass joints) with a sealed mechanical glass stirrer, an addition funnel, and a reflux condenser capped with a calcium chloride drying tube is charged with 30.0 g. (0.140 mole) of 2-methyldodecanoic acid (Note 2) and 13.7 ml. (0.144 mole) of phosphorus tribromide (Note 3). Stirring is commenced, and 14.6 ml. (0.284 mole) of dry bromine (Note 4) is introduced slowly from the addition funnel until the reaction mixture retains a deep bromine coloration. The addition requires about 10 minutes to this stage (Note 5). The remainder of the bromine is then added all at once, and the flask heated in a bath maintained at 85–90° (Note 6) for 1.5 hours. An additional 3.6 ml. (0.07 mole) of bromine is then added and the heating at 85–90° continued for 18 hours. The mixture is cooled to room temperature and poured into a 1-l. separatory funnel containing about 150 ml. of water and 200 g. of cracked ice. The transfer is completed with the addition of 150 ml. of benzene, and the separatory funnel is shaken vigorously for about 10 minutes, during which time most of the ice melts and the originally denser organic phase becomes the upper phase. The aqueous layer is separated and washed with 100 ml. of benzene, while the organic layer is vigorously shaken with another 200-ml. portion of ice water. This ice-water wash is also shaken with the 100-ml. portion of benzene and is then discarded. The combined benzene extracts are filtered through anhydrous sodium sulfate to remove suspended water; then the benzene and residual bromine are removed under reduced pressure (water aspirator) at a bath temperature of 70° or below (Note 7). The crude bromoacyl bromide is added slowly, at room temperature, to a solution of 13.7 g. (0.35 g. atom) of potassium metal (Note 1) in 300 ml. of dry *tert*-butyl alcohol (Note 1) contained in a well-dried 1-l. flask fitted with a reflux condenser that is protected from moisture with a calcium chloride drying tube. The resultant suspension is heated at reflux for 1 hour, cooled, and diluted with three volumes of water. The mixture, containing insoluble *tert*-butyl 2-methylenedodecanoate, is extracted with two 100-ml. portions of low-boiling petroleum ether (Note 8) and (Note 9). The combined petroleum ether extracts are washed with water and filtered through anhydrous sodium carbonate into a distilling flask from which the solvent is flash-distilled. The residual *tert*-butyl 2-methylenedodecanoate is then distilled through a 61-cm. Podbielniak-type column

(Note 10) at 129–130°/3.0 mm.; the yield is 18.5–21 g. of semipurified ester, n_D 1.4405–1.4413 (Note 11) and (Note 12).

The *tert*-butyl 2-methylenedodecanoate is hydrolyzed by heating under reflux with ethanolic potassium hydroxide for 6 hours; 40 ml. of 95% ethanol and 3.7 g. (0.056 mole) of 85% potassium hydroxide are used for each 10 g. (0.037 mole) of the ester. The hydrolysis mixture is cooled, diluted with three volumes of water, and extracted with two 100-ml. portions of petroleum ether which are discarded. The aqueous phase is acidified to Congo red with 5*N* sulfuric acid, and the 2-methylenedodecanoic acid is extracted with two 150-ml. portions of low-boiling petroleum ether (Note 8). These extracts are combined, washed with three 100-ml. portions of water to ensure complete removal of *tert*-butyl alcohol, and dried by filtration through anhydrous sodium sulfate. The solvent is removed by flash distillation, and the acid is subjected to rapid distillation from a Claisen flask (Note 13). 2-Methylenedodecanoic acid containing less than 5% of 2-methyl-2-dodecenoic acid is collected at 149–151°/1.7 mm., m.p. about 32°, λ_{max} 209 mμ, ε 7800, in hexane (Note 14). The yield is 10.5–12 g. (35–40% from 2-methyldodecanoic acid), not including the acid obtained on acidification of the dehydrohalogenation mixture (Note 9).

2. Notes

1. The precautions for handling potassium and the procedure for preparing anhydrous potassium *tert*-butoxide have already been described (p.132).
2. 2-Methyldodecanoic acid was prepared as follows according to the method of Cason, Allinger, and Williams.[2] A three-necked flask fitted with a sealed mechanical stirrer, dropping funnel, and efficient reflux condenser is charged with 1.4 l. of absolute ethanol; then, while stirring, 48.3 g. (2.1 g. atoms) of sodium is added gradually in small pieces. The dropping funnel is charged with 383 g. (2.2 moles) of diethyl methylmalonate (Matheson, Coleman and Bell) which is added to the sodium ethoxide solution over a period of about 20 minutes; then the mixture is boiled under reflux for 5 minutes. The dropping funnel is charged with 442 g. (2.0 moles) of *n*-decyl bromide (Eastman Kodak Company, white label brand) which is added to the mixture as rapidly as is allowed by the exothermic reaction. After the addition is complete (about 20 minutes), the mixture is boiled under reflux for 2 hours, then neutralized with a few drops of glacial acetic acid. About two-thirds of the alcohol is removed by distillation, and 2 l. of water is added to the residue. The organic phase is separated, and the aqueous phase extracted with three 250-ml. portions of benzene. The organic phase and extracts are combined, washed with water, and dried over anhydrous sodium sulfate. The residue obtained upon evaporation of the solvent is treated with a solution of 447.5 g. of 85% potassium hydroxide pellets in 3.5 l. of 95% ethanol and the mixture heated at reflux, with stirring, for 4 hours. About two-thirds of the solvent is removed by distillation, 3 l. of water is added, followed by sufficient (about 2 l.) 6*N* sulfuric acid (cooling is necessary) to bring the pH of the solution to 1–2. The organic phase is separated, and the aqueous phase (containing some precipitated sulfates) is extracted with two portions of ether. The organic phase and extracts are combined, washed with water, then with saturated sodium chloride solution, and finally dried over anhydrous sodium sulfate. The residue obtained upon evaporation of the ether is heated at 180–190°, at which temperature decarboxylation occurs smoothly over a 20-minute period. The material is then distilled from a modified Claisen flask. The yield of product, b.p. 159–161°/4.4 mm., is 262–318 g. (61–74%), n_D^{25} 1.4404–1.4408.
3. Phosphorus tribromide (Eastman Kodak Company, white label brand) was freshly distilled before use. The full molar equivalent accelerates the desired α-bromination.
4. Bromine is conveniently dried over phosphorus pentoxide, then filtered into the addition funnel through a plug of glass wool.
5. The first mole equivalent of bromine reacts with the phosphorus tribromide to form the solid pentabromide which, in turn, is rapidly consumed in the formation of the acyl bromide.
6. The temperature is critical. At lower temperatures the reaction is very slow, and at higher temperatures partial dehydrobromination and subsequent allylic bromination result in contamination of the product with dienoic acid, as evidenced by the characteristic intense absorption at 275 mμ in hexane.
7. Higher temperatures at this point tend to promote dehydrobromination under the acidic conditions with the formation of 2-methyl-2-dodecenoic acid.
8. Commercial hexane from petroleum fraction (b.p. 65–68°) is satisfactory.
9. Acidification of the alkaline aqueous layer to Congo red with 5*N* sulfuric acid liberates 2–4 g. of

crude 2-methylenedodecanoic acid which can be isolated by extraction with petroleum ether as described below. Distillation of such material gave a product which did not crystallize readily.

10. A simplified Podbielniak column[3] was employed. Other columns of comparable efficiency should be suitable.

11. If the distillation is carried out in a Claisen flask, the final product is impure, apparently contaminated with about 10% of 2-methyl-2-dodecenoic acid.

12. Pure *tert*-butyl 2-methylenedodecanoate may be isolated by refractionation of this product through an efficient column. The yield in such an experiment was 15–17 g. of material with n_D^{25} 1.4400.

13. Fractionation through a column results in some isomerization.

14. 2-Methylenedodecanoic acid, free from any isomeric impurities, can be obtained by recrystallization from acetone. The pure acid is recovered in over 70% yield, m.p. 33.3–34.2°, λ_{max} 210 mμ, ε 7500, in hexane. It is very difficult to obtain pure methylene acid from Claisen-distilled *tert*-butyl ester (cf. (Note 11)).

3. Discussion

This preparation is based on the method of Cason, Allinger, and Williams.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 608

References and Notes

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

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

petroleum ether

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

phosphorus tribromide (7789-60-8)

acetone (67-64-1)

potassium hydroxide,
potassium hydroxide pellets (1310-58-3)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

potassium (7440-09-7)

diethyl methylmalonate (609-08-5)

hexane (110-54-3)

tert-butyl alcohol (75-65-0)

2-methyldodecanoic acid (2874-74-0)

2-Methylenedodecanoic acid,
Dodecanoic acid, 2-methylene- (52756-21-5)

2-methyl-2-dodecenoic acid

n-decyl bromide (112-29-8)

phosphorus pentoxide (1314-56-3)

potassium tert-butoxide (865-47-4)

tert-butyl 2-methylenedodecanoate