Organic Syntheses

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.

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.

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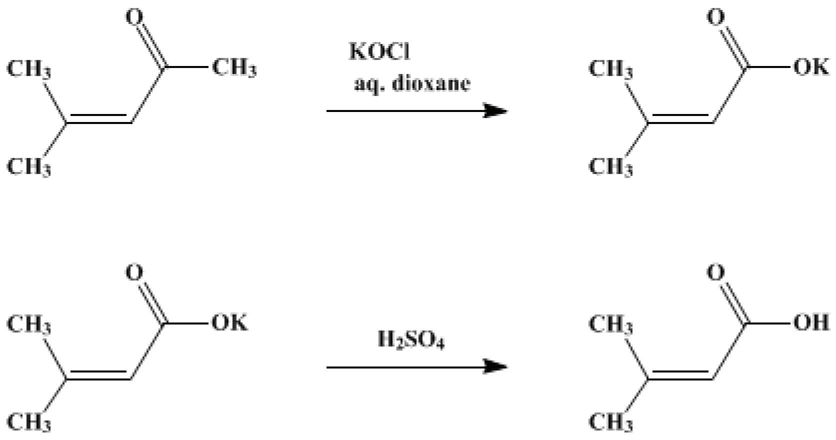
β,β-DIMETHYLACRYLIC ACID

[Senecioic acid]



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1. Procedure

A 5-l. round-bottomed three-necked flask is equipped with a Kyrides sealed stirrer and two long condensers, and the apparatus is so arranged that, if necessary, the exit water from the condensers may be quickly used to cool the flask.

In the flask are placed 200 ml. of dioxane, 100 g. (1.02 moles) of mesityl oxide, and a solution of 4.6 moles of potassium hypochlorite in 3 l. of water (Note 1), and the stirrer is started. The mixture becomes warm immediately, and within 5 minutes chloroform begins to reflux. When the reaction becomes very vigorous the stirrer is stopped and the flask is cooled with running water (Note 2). The stirring is resumed as soon as feasible and is continued for 3–4 hours, when the temperature of the mixture will have dropped to that of the room. Sodium bisulfite (about 5 g.) is then added to react with the excess hypochlorite (Note 3).

One of the condensers is then replaced by a dropping funnel, and enough 50% sulfuric acid (about 200 ml.) is added, with stirring and cooling, to make the solution acid to Congo red paper. When the solution has cooled, it is extracted with eight 400-ml. portions of ether (Note 4). The ether extract is *carefully* distilled on a steam bath until the ether and chloroform are removed.

The residue is then placed in a modified Claisen flask and distilled under reduced pressure. Dimethylacrylic acid distils at 100–106°/20 mm. The yield of white solid is 49–53 g. (49–53%). This product melts at 60–65°. It may be further purified by recrystallization from petroleum ether (b.p., 60–70°) or water (Note 5).

2. Notes

1. The hypochlorite is prepared according to *Org. Syntheses*, **17**, 66; Coll. Vol. **2**, 429 (1943), Note 2. It is cooled to 10° before it is placed in the flask.
2. The flask is cooled only as much as is necessary to keep the chloroform refluxing gently. After 30 minutes the reaction will have subsided enough so that no further cooling is necessary.
3. When a few milliliters of the solution no longer liberate iodine from a slightly acid potassium iodide solution, enough sodium bisulfite has been added.
4. It is important that the ether be *well shaken* with the solution during the extractions.
5. For recrystallization from water, 48–50 g. of the acid is dissolved in 450 ml. of hot water. The

solution is cooled in ice for several hours, and the crystalline precipitate is filtered with suction and dried overnight in a desiccator. The yield of pure dimethylacrylic acid melting at 66–67.5° is 35–40 g., a recovery of 70–83%.

3. Discussion

This acid has been prepared from various α-haloisovaleric acid derivatives by elimination of the halogen together with one of the β-hydrogen atoms;[1,2,3,4] from β-hydroxyisovaleric acid derivatives by elimination of water;[5,6,7] by action of sodium isobutoxide on iodoform;[8] by the condensation of malonic acid with acetone;[9,10,11] by the reaction of acetone and ketene;[12] by condensation of acetoacetic ester with acetone and action of barium hydroxide on the product, isopropylidene acetoacetic ester;[13] by the action of alkali upon 2,4-dibromo-2-methyl-butanone;[14] by the incomplete ozonolysis of phorone;[15] by the action of alcoholic potassium hydroxide upon 2,5,5,7-tetramethylocta-2,6-diene-4-one;[16] by the action of potassium hydroxide on isopropenylacetic acid;[17] by the action of aluminum chloride on α,α-dimethylsuccinic anhydride;[18] by metallating isobutylene with amylsodium, carbonating, and acidifying;[19] by the action of hypohalites on mesityl oxide;[20,21,22] and by the action of sulfuric acid on 3-methyl-3-butenoic acid.[23]

References and Notes

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

petroleum ether

isopropylidene acetoacetic ester

phorone

sulfuric acid (7664-93-9)

ether (60-29-7)

chloroform (67-66-3)

potassium iodide (7681-11-0)

sodium bisulfite (7631-90-5)

iodine (7553-56-2)

acetone (67-64-1)

aluminum chloride (3495-54-3)

potassium hydroxide (1310-58-3)

barium hydroxide (17194-00-2)

Mesityl oxide (141-79-7)

Ketene (463-51-4)

iodoform (75-47-8)

Malonic acid (141-82-2)

potassium hypochlorite

hypochlorite (14380-61-1)

dioxane (123-91-1)

isobutylene (9003-27-4)

β,β-Dimethylacrylic acid,
Senecioic acid (541-47-9)

Dimethylacrylic acid

β-hydroxyisovaleric acid (625-08-1)

sodium isobutoxide

2,4-dibromo-2-methyl-butanone

2,5,5,7-tetramethylocta-2,6-diene-4-one

isopropenylacetic acid,
3-methyl-3-butenoic acid (53774-20-2)

α,α-dimethylsuccinic anhydride (17347-61-4)

amylsodium