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Syntheses

A Publication
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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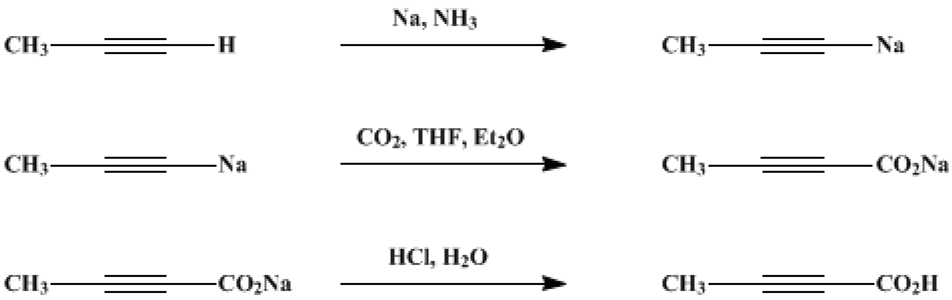
TETROLIC ACID

[2-Butynoic Acid]



Submitted by J. C. Kauer and M. Brown[1].
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1. Procedure

A 3-l., three-necked, round-bottomed flask is equipped with a glass paddle stirrer, a condenser containing a mixture of acetone and solid carbon dioxide, and a gas inlet tube. The outlet of the condenser is protected from the atmosphere by a T-tube through which a slow stream of nitrogen is passed. The flask is purged with nitrogen, and about 1.5 l. of anhydrous liquid ammonia is either poured or distilled into the flask. A small crushed crystal of ferric nitrate nonahydrate is added, followed by 23 g. (1 g. atom) of freshly cut sodium in small pieces (Note 1).

Methylacetylene (44–48 g., 1.1–1.2 mole) (Note 2) is bubbled in through the gas inlet tube with rapid stirring. Sodium methylacetylide precipitates as a flocculent gray solid. The solid carbon dioxide is removed from the condenser, and the ammonia is evaporated overnight under a slow stream of nitrogen. A hot water bath may be used to drive off residual ammonia. One liter of dry tetrahydrofuran (Note 3) and 500 ml. of anhydrous ether are added, and with rapid stirring a slow stream of anhydrous carbon dioxide from a cylinder is passed into the mixture (Note 4). After 8 hours the rate of absorption of carbon dioxide is very slow. Any solid caked on the inside walls of the flask should be scraped off with the glass paddle stirrer. A very slow flow of carbon dioxide is continued overnight (Note 5).

The solvent is removed as completely as possible by distillation on a steam bath under water-pump vacuum. Two hundred milliliters of water is added, and the solid is dissolved by swirling the flask (Note 6). The solution is filtered if suspended solid is present. The aqueous solution is extracted twice with 100-ml. portions of ether. The aqueous layer in a 1-l. Erlenmeyer flask is then cooled in ice, and a mixture of 70 ml. of concentrated hydrochloric acid and 200 g. of ice is added slowly with swirling. The acidified solution is continuously extracted with 200 ml. (or more) of ether for 24–36 hours. The extract is evaporated in a stream of air or nitrogen to give tetrolic acid in the form of a mushy tan solid that is further dried in a vacuum desiccator over concentrated sulfuric acid for 2 days (Note 7). The product is a tan crystalline solid weighing 58–60 g. (69–71% based on sodium) and melting at 71–75°. It is purified further by addition to 700 ml. of boiling hexane. As soon as the tetrolic acid has dissolved, about 1 g. of activated carbon is added, and the solution is filtered through a heated funnel (Note 8). The filtrate is refrigerated (5°) overnight and 42–50 g. (50–59%) (Note 9) of tetrolic acid is collected in the form of white needles, m.p. 76–77°. A second recrystallization from hexane gives tetrolic acid melting at 76.5–77° (Note 10).

2. Notes

1. The first few pieces of sodium should be converted to sodium amide as evidenced by a color change from blue to gray. The rest of the sodium is then added over a period of 30 minutes.
2. An excess may be used if the purity of the methylacetylene is in doubt; however, a large excess will

result in foaming when the liquid ammonia is later evaporated. Methylacetylene of satisfactory purity is available from the Matheson Company.

3. The tetrahydrofuran is distilled from sodium and stored under nitrogen.

4. When a flow rate of 70–100 ml. per minute is used, the internal temperature does not rise above 30° and most of the carbon dioxide is absorbed. A lower yield (50%) of product is obtained when carbon dioxide gas is generated by the slow evaporation of commercial solid carbon dioxide. *[Caution! See p. 976.]*

5. The reaction is complete when the addition of a small amount of the solid to a few drops of water yields a solution with a pH below 10.

6. Residual tetrahydrofuran may separate as a second (upper) phase. It is removed by the ether extraction.

7. To avoid spattering of the solid the desiccator is evacuated slowly. If drying is incomplete, an aqueous layer will be left in the hexane solution when the tetrolic acid is recrystallized.

8. Prolonged boiling should be avoided since some tetrolic acid is lost by volatilization.

9. The submitters obtained yields of tetrolic acid as high as 67.2 g. (80%).

10. In one run the submitters passed excess methylacetylene (1.6 moles) into a solution of sodium in liquid ammonia until the color turned from blue to white. No ferric nitrate was used. This somewhat shorter procedure yielded pure white sodium methylacetylide and did not diminish the yield of tetrolic acid. Excess methylacetylene is necessary because 0.5 mole is converted to propylene.

3. Discussion

Tetrolic acid has been prepared by treatment of acetoacetic ester with phosphorus pentachloride followed by dehydrochlorination of the reaction products;[2] by the base-catalyzed isomerization of 3-butynoic acid;[3] and by the treatment of 4,4-dibromo-3-methyl-2-pyrazolin-5-one with alkali followed by acidification.[4]

It has also been prepared by the carbonation of sodium methylacetylide under pressure,[5,6] in ether suspension,[7] and in the dry state.[8]

4. Merits of Preparation

The virtue of the present method is its convenience, especially when pressure equipment is not available. This method is probably generally applicable to the synthesis of acetylenecarboxylic acids from terminal acetylenes. Thus phenylpropiolic acid was prepared from phenylacetylene in 51% yield by the present procedure.

References and Notes

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

acetoacetic ester

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

phosphorus pentachloride (10026-13-8)

propylene (115-07-1)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

carbon (7782-42-5)

sodium (13966-32-0)

Phenylacetylene (536-74-3)

Phenylpropiolic acid (637-44-5)

sodium amide (7782-92-5)

Tetrahydrofuran (109-99-9)

ferric nitrate

hexane (110-54-3)

methylacetylene (74-99-7)

2-butynoic acid,
Tetrolic acid (590-93-2)

ferric nitrate nonahydrate (7782-61-8)

Sodium methylacetylide

3-butynoic acid (2345-51-9)

4,4-dibromo-3-methyl-2-pyrazolin-5-one