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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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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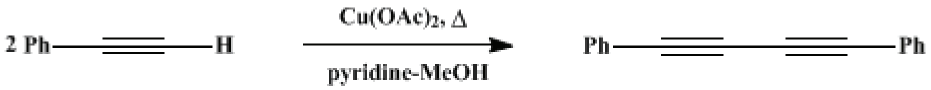
DIPHENYLDIACETYLENE

[Butadiyne, diphenyl-]



Submitted by I. D. Campbell and G. Eglinton[1].
Checked by Joanne Groves and Virgil Boekelheide.

1. Procedure

To a saturated solution of 5.5 g. (0.028 mole) of finely powdered cupric acetate monohydrate (Note 1) in 20 ml. of a 1:1 by volume pyridine-methanol mixture (Note 2), (Note 3), (Note 4), and (Note 5) contained in a 50-ml. round-bottomed flask fitted with a reflux condenser is added 2.0 g. (0.0196 mole) of phenylacetylene (Note 6). The deep-blue suspension becomes green when heated under reflux. After 1 hour of heating, the solution is cooled (Note 7) and added dropwise to 60 ml. of 18*N* sulfuric acid, with stirring and external cooling in an ice-salt freezing mixture (Note 8). The resulting white suspension is extracted with three 25-ml. portions of ether, and the combined ethereal extracts are washed with 15 ml. of aqueous ethanolic silver nitrate solution (Note 9) to remove any unchanged phenylacetylene. The ether solution is then washed twice with water and dried over anhydrous magnesium sulfate. When the dried ether solution is concentrated under reduced pressure, a brown oil (1.81 g.) remains which solidifies on cooling.

The crude solid is purified by dissolving it in 50 ml. of petroleum ether (b.p. 40–60°) and introducing it on a short alumina column (15 g., Brockmann Activity 1 or an equivalent chromatographic alumina). The column is then eluted with 300 ml. of a 1:9 mixture of ether-petroleum ether (b.p. 40–60°). Concentration of the eluate leaves a solid which is recrystallized from aqueous ethanol to give 1.4–1.6 g. (70–80%) of diphenyldiacetylene as large colorless needles, m.p. 87–88° (Note 10).

2. Notes

1. Commercially available crystalline cupric acetate monohydrate was used. A large excess of cupric acetate does not improve the yield. Small catalytic amounts can be used if the cupric salt is continually regenerated by passage of oxygen through the reaction mixture, but the procedure is much slower.
2. A good grade of commercial pyridine was used. The reaction can also be carried out under anhydrous conditions (anhydrous cupric acetate, anhydrous methanol); then the pyridine is distilled from potassium hydroxide pellets. The yields are similar, and, in fact, water may be added as co-solvent if desired.
The solubility of anhydrous cupric acetate is ca. 2.3 g. per 100 ml. of pyridine, and that of the hydrate is ca. 1.6 g. per 100 ml. of pyridine. The solubility is much improved by the addition of methanol (solubility ca. 8.6 g. per 100 ml. of a 1:1 mixture of pyridine-methanol).
For high-dilution experiments, for example, the cyclization of α,ω-diynes, about 4 volumes of ether per volume of reagent solution can be added as entraining solvent without precipitation of the copper salt. A lower reaction temperature results.
3. Commercial grade methanol was used. Methanol is best avoided in experiments involving esters, as methanolysis has been encountered.[2]
4. It is apparently not essential that all the cupric acetate be in solution. Large volumes of solvent ensure complete solution but are inconvenient during isolation of the product.
5. Other solvent systems have been investigated. A base appears to be essential to remove the acetic acid formed; otherwise insoluble yellow precipitates of the cuprous derivative are obtained, which are only slowly oxidized to the required product.
6. Redistilled commercial phenylacetylene, titrating as 98% with silver nitrate-sodium hydroxide,[3] was used.

7. The reaction can be followed by adding an aliquot to ethanolic silver nitrate solution (Note 9). The reaction is complete when no precipitate of the silver derivative is obtained. Also the disappearance of the infrared absorption band at 3300 cm.$^{-1}$ (3.03 μ) (ethynyl νCH) can be followed with carbon tetrachloride extracts of aliquots.

An 89% yield of diphenyldiacetylene was obtained when the reaction was allowed to proceed for 24 hours at room temperature (20°).

8. This is more convenient than removing the pyridine and the methanol by distillation.

9. The reagent is made by dissolving 3.5 g. of silver nitrate in 5 ml. of water and adding 10 ml. of ethanol.

10. The product may be contaminated by traces of the corresponding eneyne, *trans*-1,4-diphenyl-but-1-en-3-yne, formed by Straus coupling.[4] This compound, however, has an ultraviolet absorption spectrum which differs markedly from that of diphenylbutadiyne.[5]

3. Discussion

This compound has been prepared by air oxidation of the preformed cuprous salt[6] and through use of aqueous cuprous chloride-ammonium chloride and an oxidant (e.g., oxygen).[3] More recently the compound has been prepared in 95% yield by oxidation of phenylacetylene in pyridine solution containing cuprous chloride[7] and in 97% yield by oxidation in tetramethylenediamine solution containing 5 mole percent cuprous chloride.[8] These and other coupling procedures have been reviewed.[9,10,11]

4. Merits of the Preparation

The reaction, "Glaser oxidative coupling," is a general one,[9] but this particular technique is recommended for the more water-insoluble ethynyl compounds, and also for the cyclization of α,ω-diynes,[2,12] where controlled dilution is required.

The cupric acetate-pyridine reagent provides a homogenous and basic reaction medium. The yields are high, and there is seldom precipitation of the cuprous derivative which may slow down the cuprous chloride-oxygen procedure.[3]

The rate of oxidative coupling is said to decrease with decreasing acidity of the ethynyl hydrogen.[13] Thus oct-1-yne underwent only limited reaction after being heated with the reagent under reflux for 24 hours.

It is to be noted that cupric acetate has been used to oxidize other systems, for example, α-ketols, phenols, thiols, and nitroalkanes.

References and Notes

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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)

methanol (67-56-1)

ether (60-29-7)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

silver nitrate (7761-88-8)

oxygen (7782-44-7)

carbon tetrachloride (56-23-5)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

cuprous chloride (7758-89-6)

cupric acetate (142-71-2)

Phenylacetylene (536-74-3)

magnesium sulfate (7487-88-9)

cupric acetate monohydrate (6046-93-1)

Diphenyldiacetylene,
Butadiyne, diphenyl-,
diphenylbutadiyne (886-66-8)

tetramethylenediamine (110-60-1)

oct-1-yne (629-05-0)

trans-1,4-diphenyl-but-1-en-3-yne