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.

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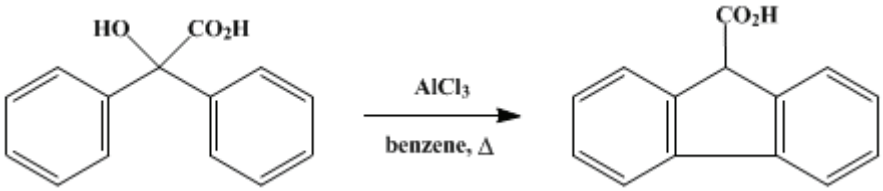
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.033.0037

Organic Syntheses, Coll. Vol. 4, p.482 (1963); Vol. 33, p.37 (1953).

9-FLUORENECARBOXYLIC ACID

[Fluorene-9-carboxylic acid]



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1. Procedure

Caution! Because of the evolution of considerable amounts of hydrogen chloride, this preparation must be conducted in a good hood or the apparatus must be attached to a gas trap.

A mixture of 45.6 g. (0.2 mole) of benzilic acid (Note 1) in 700 ml. of anhydrous thiophene-free benzene, contained in a 2-l. three-necked flask fitted with a reflux condenser (attached to a calcium chloride drying tube) and a motor-driven sealed stirrer, is cooled in an ice bath until a crystalline mass results. To the stirred mixture is added, in one portion, 80 g. (0.6 mole) of anhydrous aluminum chloride. The stirred mixture is heated until refluxing begins and is maintained at this temperature for 3 hours. During this period much hydrogen chloride is evolved, and the initially yellow solution soon becomes deep red. The solution is cooled and decomposed by the cautious addition of small pieces of ice, and then 400 ml. of water is added cautiously, followed by 200 ml. of concentrated hydrochloric acid. The benzene is removed by steam distillation, and the product is separated by filtration from the hot mixture. The lumps of product are crushed and extracted with 400 ml. of boiling 10% sodium carbonate solution. The mixture is filtered, and the extraction is repeated on the undissolved residue with an additional 200 ml. of hot 10% sodium carbonate solution. The basic filtrates are combined, 3–4 g. of Norit is added, and the mixture is heated to boiling. The Norit is separated by filtration, and the cooled solution is strongly acidified with cold concentrated hydrochloric acid (Note 2). The solid is collected on a Büchner funnel, washed with two 100-ml. portions of water, and dried (Note 3). The 9-fluorenecarboxylic acid so obtained weighs 39–41 g. (93–97%) and melts at 215–222°.

This product can be further purified by stirring it for several minutes with 200 ml. of benzene at 45°. The insoluble portion is collected on a Büchner funnel and washed first with 40 ml. of cold benzene and then with 40 ml. of petroleum ether (b.p. 28–38°). There is thus obtained 30–34 g. (71–81%) of almost colorless 9-fluorenecarboxylic acid melting at 219–222° with some previous sintering (Note 4).

2. Notes

1. The Distillation Products Industries grade melting at 150–151° is satisfactory.
2. Good results are usually obtained if the temperature during neutralization is not allowed to exceed 15°.
3. If the occluded hydrochloric acid and aluminum salts are effectively removed during the washing operation, this product can be dried in a steam oven without discoloration.
4. The melting points reported for this compound range from 210° to 230°[2,3,4,5,6] and appear to be a function of the rate of heating. The product obtained above, showing a neutralization equivalent of 215–218 (calculated 210), has proved very satisfactory. The acid may be further purified by crystallization from 50% ethanol using 5–6 ml./g. There is then obtained 60–70% of acid melting at 221–223° with some previous sintering. All melting points are uncorrected.

3. Discussion

The procedure described is essentially that of Arnold, Parham, and Dobson[2] based on the reaction reported by Vorlander and Pritzsche.[3] This acid has also been prepared from ethyl trichloroacetate in benzene with aluminum chloride,[4] from fluorene by metalation with *n*-butyllithium,[5,6] sodium triphenylmethyl,[7] lithium triphenylgermanium,[8] lithium in tetrahydrofuran,[9] phenyllithium,[6] *o*-tolyllithium,[6] mesityllithium,[6] potassium hydroxide,[10] or ethylsodium-diethylzinc complex followed by carbonation,[11] from diphenyleneketene and water,[12] and from 9-fluorenylmagnesium bromide and carbon dioxide.[13]

References and Notes

1. Hamline University, St. Paul, Minnesota.
2. Arnold, Parham, and Dodson, *J. Am. Chem. Soc.*, **71**, 2439 (1949).
3. Vorlander and Pritzsche, *Ber.*, **46**, 1793 (1913).
4. Delacre, *Bull. soc. chim. France*, [3] **27**, 875 (1902).
5. Burtner and Cusic, *J. Am. Chem. Soc.*, **65**, 262 (1943).
6. Morton, *Iowa State Coll J. Sci.*, **28**, 367 (1954) [*C. A.*, **49**, 8162 (1955)].
7. Schlenk and Bergmann, *Ann.*, **463**, 98 (1928).
8. Gilman and Gerow, *J. Org. Chem.*, **23**, 1582 (1958).
9. Gilman and Gorsich, *J. Org. Chem.*, **23**, 550 (1958).
10. Morton, Claff, and Kagen, *J. Am. Chem. Soc.*, **76**, 4556 (1954).
11. Ludwig and Schulze, *J. Org. Chem.*, **24**, 1573 (1959).
12. Staudinger, *Ber.*, **39**, 3064 (1906).
13. Grignard and Courtot, *Compt. rend.*, **152**, 1493 (1911).

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

petroleum ether

sodium triphenylmethyl

lithium triphenylgermanium

ethylsodium-diethylzinc complex

ethanol (64-17-5)

hydrogen chloride,
hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium carbonate (497-19-8)

aluminum (7429-90-5)

carbon dioxide (124-38-9)

Norit (7782-42-5)

aluminum chloride (3495-54-3)

Benzilic acid (76-93-7)

potassium hydroxide (1310-58-3)

Phenyllithium (591-51-5)

lithium (7439-93-2)

fluorene (86-73-7)

n-butyllithium (109-72-8)

Tetrahydrofuran (109-99-9)

9-FLUORENECARBOXYLIC ACID,
Fluorene-9-carboxylic acid (1989-33-9)

ethyl trichloroacetate (515-84-4)

diphenyleneketene

9-fluorenylmagnesium bromide

mesityllithium

o-Tolyllithium