



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.

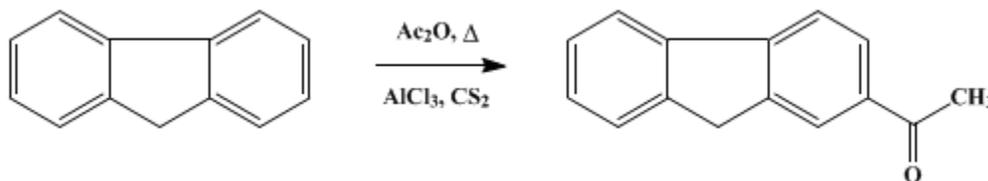
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.23 (1955); Vol. 28, p.3 (1948).

2-ACETYLFUORENE

[Ketone, 2-fluorenyl methyl]



Submitted by F. E. Ray and George Rieveschl, Jr..

Checked by R. L. Shriner and Arne Langsjoen.

1. Procedure

Caution! Carbon disulfide, used as a solvent in this preparation, is highly inflammable; its vapor may ignite on contact with a hot laboratory steam line.

A 1-l. three-necked round-bottomed flask is fitted with a dropping funnel, a reflux condenser attached to a hydrogen chloride absorption trap,¹ and a very sturdy mechanical stirrer (Note 1), which may be of the mercury-sealed or rubber-sleeve type. In the flask are placed 350 ml. of dry carbon disulfide and 80 g. (0.48 mole) of fluorene (Note 2). The stirrer is started, and, after the fluorene has dissolved, 128 g. (0.96 mole) of anhydrous aluminum chloride is added in one portion. In the dropping funnel is placed 49.4 g. (0.48 mole) of redistilled acetic anhydride, and about 1 ml. of it is added dropwise to the vigorously stirred dark red reaction mixture. If the reaction does not start immediately it is initiated by warming the reaction flask in a water bath (Note 3). After the reaction has started, the balance of the acetic anhydride is added at such a rate that the carbon disulfide refluxes gently; about 45–55 minutes is required. When approximately one-half of the acetic anhydride has been added an addition complex separates as a heavy mass which makes stirring very difficult. However, stirring must be maintained to prevent excessive local reaction at the point of introduction of the acetic anhydride. The mixture is stirred and refluxed on the water bath for an hour after the addition of the acetic anhydride is complete.

The dark green mass is collected on a large Büchner funnel and transferred as quickly as possible (Note 4) to a 1-l. beaker in which it is stirred mechanically for 10 minutes with 300 ml. of carbon disulfide (Note 5). The solid is again collected and washed on the filter with two 50-ml. portions of carbon disulfide (Note 6) and with one 100-ml. portion of petroleum ether (b.p. 28–35°). The resulting granular aluminum chloride complex is decomposed by portionwise addition to a well-stirred mixture of 800 ml. of water and 30 ml. of concentrated hydrochloric acid in a 2-l. beaker under a hood. Each portion is allowed to hydrolyze before the next is added. The hydrolysis mixture should not be cooled. The crude 2-acetylfluorene is collected on a filter and washed three times with 100-ml. portions of water. After drying in an oven at 100° for 3 hours the light-orange ketone weighs 83–95 g. (83–95%) and melts over the range 113–117° (Note 7). This crude product is transferred to a 2-l. round-bottomed flask containing 800 ml. of 95% ethanol and 5 g. of decolorizing carbon. The mixture is refluxed for 1 hour and filtered hot. On cooling the filtrate deposits 71–83 g. of light-tan solid melting at 120–123°. A second recrystallization from 800 ml. of ethanol yields 55–63 g. (55–63%) of a light-cream-colored powder which melts at 124–126° and which is pure enough for most purposes (Note 8).

2. Notes

1. The stirrer, which may be of either the half-round or the propeller type, must be of heavy construction and must be driven by one of the more powerful laboratory stirring motors. Agitation must be maintained throughout the reaction period.
2. If technical fluorene (m.p. 103–107°) from Eastman Kodak Company or the Barrett Company is

used, much difficulty is experienced in the purification of the product. Technical fluorene can be rendered suitable for the preparation by recrystallization from hot 95% ethanol (1 l. for 150 g.). The once-recrystallized material melts at 114–115° (lit. 116°).

3. It is necessary to make sure that the reaction has started before the addition of more acetic anhydride in order to prevent a violent reaction.

4. Exposure to the air causes the addition product to become sticky and difficult to handle.

5. Unless this operation can be conducted at a point remote from flames, hot plates, and other sources of heat, a flask should be substituted for the open beaker.

6. The carbon disulfide extracts unchanged fluorene and other impurities. Any lumps in the crude material should be crushed during the first washing. The rinsing with petroleum ether removes the last of the carbon disulfide.

7. This crude 2-acetylfluorene is completely soluble in carbon disulfide and thus is free of the insoluble 2,7-diacetylfluorene. It may be used directly for the oxidation to fluorenone-2-carboxylic acid (p. 420).

8. The pure product² melting at 128–129° (cor.) can be obtained in 42–45% yield by two more recrystallizations from 400-ml. portions of acetone. Pure 2-acetylfluorene has also been reported³ as melting at 132°, but this value has not been checked.

3. Discussion

2-Acetylfluorene has been prepared by the reaction of fluorene with acetic anhydride^{2,4} or with acetyl chloride^{3,5} in the presence of aluminum chloride in carbon disulfide or in nitrobenzene. When nitrobenzene is employed as the solvent it must be removed by a time-consuming steam distillation, and the use of acetyl chloride as a reagent agent leads to the formation of considerable amounts of 2,7-diacetylfluorene.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 420](#)

References and Notes

1. *Org. Syntheses Coll. Vol. 2, 4* (1943).
2. Bachmann and Sheehan, *J. Am. Chem. Soc.*, **62**, 2687 (1940).
3. Dziewonski and Schnayder, *Bull. intern. acad. polon. sci.*, **1930A**, 529 [*C. A.*, **25**, 5416 (1931)].
4. Ray and Rieveschl, *J. Am. Chem. Soc.*, **65**, 836 (1943); Buu-Hoi and Cagniant, *Bull. soc. chim. France*, **1946**, 131.
5. Ardashev, Lomovatskaya, and Kacher, *J. Applied Chem. U.S.S.R.*, **11**, 1344 (1938) [*C. A.*, **33**, 5844 (1939)].

Appendix

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

petroleum ether

aluminum chloride complex

[ethanol](#) (64-17-5)

[hydrochloric acid](#) (7647-01-0)

acetic anhydride (108-24-7)

acetyl chloride (75-36-5)

acetone (67-64-1)

decolorizing carbon (7782-42-5)

aluminum chloride (3495-54-3)

Nitrobenzene (98-95-3)

carbon disulfide (75-15-0)

fluorene (86-73-7)

2-Acetylfluorene,
Ketone, 2-fluorenyl methyl (781-73-7)

2,7-diacetylfluorene (39665-89-9)

Fluorenone-2-carboxylic acid (784-50-9)