



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.

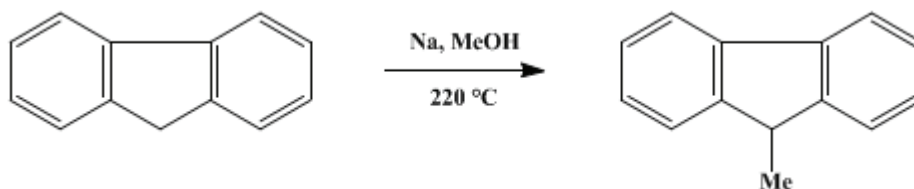
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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9-METHYLFLUORENE

[Fluorene, 9-methyl-]



Submitted by Kurt L. Schoen and E. I. Becker¹.

Checked by William S. Johnson and V. B. Haarstad.

1. Procedure

An 850-ml. steel bomb is charged with a solution of 23 g. (1.0 g. atom) of sodium in 450 ml. of absolute methanol and 113 g. (0.68 mole) of fluorene (Note 1). The vessel is then closed, heated to 220° (Note 2), and rocked for 16 hours (Note 3). The reaction vessel is allowed to cool, and the contents are transferred to a 2-l. beaker with the aid of small volumes of benzene and then water to complete the transfer. The reaction mixture is diluted with an equal volume of water, neutralized with concentrated hydrochloric acid, and extracted with three 150-ml. portions of benzene. The combined benzene extracts are washed with three 200-ml. portions of water, and the solvent is removed by distillation at atmospheric pressure. The residue is recrystallized from methanol (1 l. per 100 g. of solute) to give 96–106 g. (78–86% yield) (Note 4) of colorless 9-methylfluorene, m.p. 44–45° (Note 5).

2. Notes

1. A commercial grade of fluorene was purified by crystallization from methanol until the m.p. was 113–114°.

2. In the checkers' experience the temperature must not be below 220° or a diminution in yield will result.

3. Without rocking, the crude product is colored and the yield is slightly lower.

4. This is a total yield of material obtained in 2–3 crops. In a typical run the first crop amounted to 90 g., m.p. 44–45°, and the second, obtained on concentrating and cooling the mother liquor, amounted to 16 g., m.p. 44–45°.

The crude product may alternatively be purified by rapid distillation at reduced pressure to give 114–116 g., b.p. 95–100°/1 mm. Redistillation affords 102–105 g. (83–86% yield), b.p. 96–98°/0.6 mm., of colorless 9-methylfluorene which solidifies.

5. The submitters state that the procedure is general and has been carried out with normal alcohols from C₁ to C₇. In an analogous procedure 10 g. of fluorene was treated with 40 ml. of alcohol and 2.3 g. of sodium (in a Carius tube) to give 52–84% of redistilled 9-alkylfluorene. 9-*n*-Octadecylfluorene was prepared from 13.3 g. of fluorene, 16.2 g. of *n*-octadecyl alcohol, and 2 g. of sodium. In this case the reaction was carried out in a flask (equipped with a condenser) that was heated in an oil bath for 16 hours at 210°. The solid product was purified by crystallization.

Product	B.P./1 mm.	n_D^{25}	d_4^{25}	Yield, %
9-Ethylfluorene	123–124°	1.61801.0508		84
9- <i>n</i> -Propylfluorene	126–128°	1.60501.0326		72
9- <i>n</i> -Butylfluorene	140°	1.59561.0197		78
9- <i>n</i> -Pentylfluorene	144–146°	1.59291.0153		66
9- <i>n</i> -Hexylfluorene	156–158°	1.57570.9900		68
9- <i>n</i> -Heptylfluorene	163–165°	1.57170.9827		58

3. Discussion

Generally, **fluorene** has been alkylated in the 9-position by reaction of 9-acyl- or ester-substituted fluorenes with sodium alkoxide and an alkyl halide followed by removal of the activating group, by treating a 9-fluorenyl organometallic compound with an alkyl halide, by reduction of a 9-fluorenylidene derivative, by hydrogenolysis of a 9-alkyl-9-hydroxyfluorene, by hydrogenolysis of a 9-halogen-9-alkylfluorene, and by cyclization of a diphenylalkylcarbinol with **phosphorus pentoxide**.² The present procedure is based on the method of Shoen and Becker.³

9-Methylfluorene has been prepared by cleavage of **ethyl 9-methyl-9-fluorenylglyoxylate**,⁴ by the decarboxylation of **9-methylfluorene-9-carboxylic acid**,⁴ by the decarboxylation of **9-fluorenylacetic acid**,⁵ by the cleavage of **9-methyl-9-acetylfluorene** with alcoholic **potassium hydroxide** or soda-lime,⁶ by the reduction of **9-methyl-9-fluorenyl** with **hydriodic acid** in **acetic acid**,⁷ by the reaction of **9-fluorenyllithium**⁸ or -sodium⁹ with **methyl iodide** or **methyl sulfate**,⁹ by the cyclization of **diphenylmethylcarbinol** over **platinum-on-carbon** at 300°,¹⁰ by the reaction of **ethyl 9-methoxymethyl-9-fluorenylcarboxylate**,¹¹ by the diazotization and heating of **2-ethyl-2-aminobiphenyl**,¹² by the dehydration and then reduction of **9-methyl-9-fluorenyl**,¹³ by the thermal decomposition of **tetramethylammonium 9-fluorenyl**,¹⁴ and by recovery from coal tar.¹⁵

References and Notes

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Appendix

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

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

methanol (67-56-1)

platinum (7440-06-4)

carbon (7782-42-5)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

hydriodic acid (10034-85-2)

Methyl iodide (74-88-4)

methyl sulfate (75-93-4)

fluorene (86-73-7)

9-Methylfluorene,
Fluorene, 9-methyl- (2523-37-7)

9-Ethylfluorene (2294-82-8)

ethyl 9-methyl-9-fluorenylglyoxylate

9-methylfluorene-9-carboxylic acid

9-fluorenylacetic acid (6284-80-6)

9-methyl-9-acetylfluorene

9-methyl-9-fluorenol

9-fluorenyllithium

diphenylmethylcarbinol (1883-32-5)

ethyl 9-methoxymethyl-9-fluorenylcarboxylate

2-ethyl-2-aminobiphenyl

tetramethylammonium 9-fluorenyl

phosphorus pentoxide (1314-56-3)

9-n-Octadecylfluorene

n-octadecyl alcohol (112-92-5)

9-n-Propylfluorene

9-n-Butylfluorene

9-n-Pentylfluorene

9-n-Hexylfluorene

9-n-Heptylfluorene