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.

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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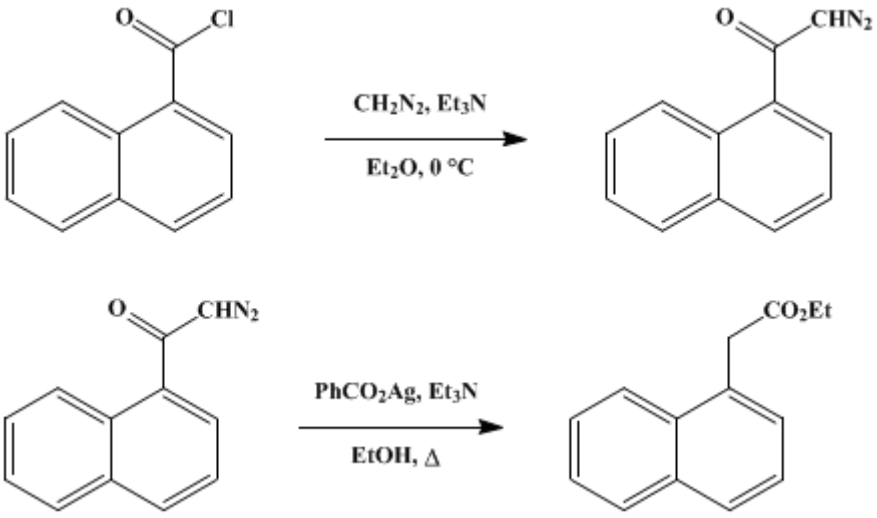
Organic Syntheses, Coll. Vol. 6, p.613 (1988); Vol. 50, p.77 (1970).

ETHYL 1-NAPHTHYLACETATE

[1-Naphthaleneacetic acid, ethyl ester]



Submitted by Ving Lee and Melvin S. Newman[1].
Checked by Gordon F. Hambly and Peter Yates.

1. Procedure

*Caution! Diazomethane is hazardous. Follow the directions for its safe handling given in Org. Synth., **Coll. Vol. 4**, 250 (1963) and **Coll. Vol. 5**, 351 (1973). The intermediate, 1-(diazoacetyl) naphthalene, is a very strong skin irritant.*

A. 1-(*Diazoacetyl)naphthalene*. A solution of 30.5 g. (0.160 mole) of 1-naphthoyl chloride (Note 1) and (Note 2) in 50 ml. of dry diethyl ether (Note 3) is added over 30 minutes to a magnetically stirred, ice-cooled solution of 6.72 g. (0.160 mole) of diazomethane [*Org. Synth.*, **Coll. Vol. 2**, 165 (1943); (Note 4)] and 16.1 g. (0.160 mole) of dry triethylamine (Note 5) in 900 ml. of dry ether. The mixture is stirred for 3 hours in the cold, and the triethylamine hydrochloride, removed by filtration, is washed twice with 30–50 ml. portions of dry ether (Note 6). The ether is removed from the combined filtrate and washings on a rotary evaporator. The yellow solid residue is dissolved in 75 ml. of dry ether, and the solution is cooled with an acetone–dry-ice mixture. The solid deposited is collected by filtration on a glass fritted-disk funnel, and the adhering ether is removed under reduced pressure as the temperature is allowed to reach room temperature, giving 26.6–28.8 g. (85–92%) of yellow 1-(diazoacetyl) naphthalene, m.p. 52–53° (Note 7) and (Note 8).

B. *Ethyl 1-naphthylacetate*. A solution of 15.7 g. (0.0801 mole) of 1-(diazoacetyl)naphthalene in 50 ml. of absolute ethanol is placed in a 100-ml., two-necked flask equipped with a Teflon-coated magnetic stirring bar, a serum stopper cap, and a reflux condenser connected to a gas-collecting device. The solution is heated to reflux, and 1 ml. of a freshly prepared catalyst solution made by dissolving 1 g. of silver benzoate (Note 9) in 10 ml. of triethylamine is added by injection through the serum cap. Evolution of nitrogen occurs and the mixture turns black. Addition of a second milliliter of catalyst solution is made when the evolution of nitrogen almost stops. This procedure is continued until further additions cause no further evolution of nitrogen (Note 10). The reaction mixture is refluxed for 1 hour, cooled, and filtered. The solvents are removed from the filtrate on a rotary evaporator. The residue is taken up in 75 ml. of ether, and the solution is washed twice in turn with aqueous 10% sodium carbonate, water, and saturated brine. Each aqueous extract is extracted with ether, and the combined ethereal extracts and solution are dried by filtration through anhydrous magnesium sulfate. After

removal of the ether, distillation affords 14.4–15.8 g. (84–92%) of colorless ethyl 1-naphthylacetate, b.p. 100–105° (0.1–0.2 mm.) (Note 11).

2. Notes

1. The submitters prepared pure 1-naphthoyl chloride, b.p. 95–96° (0.2 mm.), from pure 1-naphthoic acid in 95% yield by treatment with thionyl chloride or phosphorus pentachloride. The 1-naphthoic acid used was prepared by carbonation of 1-naphthylmagnesium bromide. As commercial 1-bromonaphthalene is impure, fractionation through a 17 × 600 mm. column is needed to obtain pure 1-bromonaphthalene, b.p. 105–108° (0.1–0.2 mm.), as indicated by GC.
2. The checkers prepared 1-naphthoyl chloride by treatment of 1-naphthoic acid, m.p. 157–161°, obtained from Aldrich Chemical Co., with phosphorus pentachloride.
3. All dry ether used was freshly distilled from ethylmagnesium bromide.
4. Solutions of diazomethane in ether were titrated with benzoic acid.
5. Triethylamine was dried by storage over anhydrous barium oxide.
6. About 90% of the theoretical yield of triethylamine hydrochloride is obtained.
7. This compound is a severe skin irritant; hence, great care should be exercised to avoid any contact. For best yields this crystallization is recommended, since the yield of ethyl 1-naphthylacetate is reduced by about 20% if the crude product is used in the rearrangement step. A sample of crystallized 1-(diazoacetyl) naphthalene, m.p. 52–53°, that had been stored in a screw-top bottle in a refrigerator for about 2 weeks afforded the same yield of ethyl 1-naphthylacetate as a freshly prepared sample.
8. The checkers obtained 26.1–26.5 g. (83–84.5%) of 1-(diazoacetyl) naphthalene, m.p. 47–49.5°, when 1-naphthoyl chloride prepared from commercial 1-naphthoic acid was used (cf. (Note 1) and (Note 2)). Recrystallization from hexane gave 24.6 g. (78%) of 1-(diazoacetyl)naphthalene, m.p. 49.5–52°, that was used in Part B.
9. The silver benzoate was made by reaction of silver nitrate with sodium benzoate in water. The submitters dried the silver benzoate and recrystallized it from *N*-methylpyrrolidone or *N,N*-dimethylformamide. The checkers dried it in an oven at 130° for 1 hour immediately before use, but did not recrystallize it. Any precipitate present after dissolving the silver benzoate in triethylamine is removed by filtration or centrifugation.
10. Usually 3–4 additions are required. The total time of reaction should not be more than 45 minutes. The checkers added the catalyst solution in 0.5-ml. portions; nitrogen evolution was initially very vigorous, and only four such additions were required.
11. When propanol is used instead of ethanol, comparable results are obtained: propyl 1-naphthylacetate, b.p. 115–118° (0.1–0.2 mm.).

3. Discussion

Ethyl 1-naphthylacetate has been prepared by ethanolysis of 1-naphthylacetonitrile under acidic conditions[2] and by the Arndt-Eistert reaction of 1-(diazoacetyl)naphthalene with ethanol and silver oxide.[3]

The method described here represents a modified Arndt-Eistert reaction as developed by Newman and Beal,[4] gives results that are more reproducible than those of the original Arndt-Eistert reaction and, in general, allows the rearrangement to be carried out successfully on larger-scale runs. The use of triethylamine in the formation of diazo ketones makes possible the use of only one equivalent of diazomethane.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 426

References and Notes

1. Evans Chemistry Laboratory, Ohio State University, Columbus, Ohio 43210.

2. M. Julia and M. Baillargé, *Bull. Soc. Chim. Fr.*, 928 (1957).
3. F. Arndt and B. Eistert, *Ber. Dtsch. Chem. Ges.*, **68**, 200 (1935).
4. M. S. Newman and P. F. Beal III, *J. Am. Chem. Soc.*, **72**, 5163 (1950).
5. M. S. Newman and P. F. Beal III, *J. Am. Chem. Soc.*, **71**, 1506 (1949).

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

brine

ethanol (64-17-5)

ether,
diethyl ether (60-29-7)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

silver oxide (20667-12-3)

silver nitrate (7761-88-8)

sodium carbonate (497-19-8)

barium oxide

nitrogen (7727-37-9)

Benzoic acid (65-85-0)

sodium benzoate (532-32-1)

1-bromonaphthalene (90-11-9)

propanol (71-23-8)

Triethylamine hydrochloride (554-68-7)

ethylmagnesium bromide (925-90-6)

magnesium sulfate (7487-88-9)

Diazomethane (334-88-3)

1-Naphthoic acid (86-55-5)

1-naphthoyl chloride (879-18-5)

N,N-dimethylformamide (68-12-2)

hexane (110-54-3)

triethylamine (121-44-8)

N-methylpyrrolidone (872-50-4)

Ethyl 1-naphthylacetate (3121-70-8)

1-Naphthaleneacetic acid, ethyl ester (2122-70-5)

1-(diazoacetyl) naphthalene,
1-(Diazoacetyl)naphthalene (4372-76-3)

silver benzoate (532-31-0)

1-naphthylmagnesium bromide

propyl 1-naphthylacetate

1-naphthylacetonitrile (132-75-2)