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.

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AZIRIDINES FROM β-IODOCARBAMATES: 1,2,3,4-TETRAHYDRONAPHTHALENE(1,2)IMINE

[1*H*-Naphth[1,2-*b*]azirine, 1a,2,3,7b-tetrahydro-]

Submitted by C. H. Heathcock[1] and A. Hassner[2].
Checked by William G. Kenyon and Richard E. Benson.

1. Procedure

A 500-ml., round-bottomed flask equipped with a reflux condenser is charged with a solution of 25 g. of potassium hydroxide in 250 ml. of 95% ethanol, to which is added 16.6 g. (0.0498 mole) of methyl (*trans*-2-iodo-1-tetralin)carbamate (Note 1). The resulting mixture is heated under reflux on a stream bath for 2 hours, cooled, and added to 500 ml. of water. The clear, yellow solution is shaken three times with 100-ml. portions of diethyl ether. The ether layers are combined, washed three times with 125-ml. portions of water and once with 125 ml. of a saturated sodium chloride, dried over 5 g. of anhydrous potassium carbonate, and filtered. The ether is removed by distillation on a steam bath, giving the crude imine as a yellow-brown oil (Note 2). The oil is transferred to a small flask, the container is rinsed with ether, and the rinse is added to the distillation flask. The product is collected by distillation through a small Vigreux column with warm water circulating through the condenser to prevent crystallization of the product. The fraction boiling at 80–82° (0.15–0.25 mm.) is collected as a solid that forms in the receiver, yielding 4.9–5.1 g. (68–70%) of the imine, m.p. 54–56° (Note 2); the IR spectrum has a band at 3205 $cm.^{-1}$ (NH) (Note 3).

2. Notes

1. The methylcarbamate may be prepared by the procedure in *Org. Synth.*, **Coll. Vol. 6**, 795 (1988).
2. The submitters state that product, m.p. 49–51°, can be obtained by direct crystallization of the oil. The oil from a run conducted on a scale twice that described above is cooled to −15° and 30 ml. of pentane is added. Upon scratching the flask, the product crystallizes, is collected by filtration, and washed with a little cold pentane, yielding 9–10 g. (62–69%), m.p. 49–51°.
3. The ^1H NMR spectrum (CCl_4) shows a broad singlet centered at δ 0.7 (1H) and complex multiplets at 1.1–3.05 (6H) and 6.76–7.30 (4H).

3. Discussion

The procedure reported here, that of Hassner and Heathcock,[3] is more convenient than the Wenker synthesis of aziridines[4] and appears to be more general.[5] It represents a simple route from olefins to aziridines (*via* β-iodocarbamates).[3,5,6] Aziridines are also useful as intermediates in the synthesis of amino alcohols and heterocyclic systems.[5,7,8,9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 795

References and Notes

1. Department of Chemistry, University of California, Berkeley, California 94720.
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3. A. Hassner and C. Heathcock, *Tetrahedron*, **20**, 1037 (1964).
4. O. E. Paris and P. E. Fanta, *J. Am. Chem. Soc.*, **74**, 3007 (1952).
5. A. Hassner and C. Heathcock, *J. Org. Chem.*, **30**, 1748 (1965).
6. G. Drefahl and K. Ponsold, *Chem. Ber.*, **93**, 519 (1960).
7. H. W. Heine, *Angew. Chem.*, **74**, 772 (1962) [*Angew. Chem. Int. Ed. Engl.*, **1**, 528 (1962)].
8. A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967).
9. L. A. Paquette and D. E. Kuhla, *Tetrahedron Lett.*, 4517 (1967).

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

β-IODOCARBAMATES

ethanol (64-17-5)

potassium carbonate (584-08-7)

ether,
diethyl ether (60-29-7)

sodium chloride (7647-14-5)

potassium hydroxide (1310-58-3)

Pentane (109-66-0)

methylcarbamate

1,2,3,4-Tetrahydronaphthalene(1,2)imine,
1H-Naphth[1,2-b]azirine, 1a,2,3,7b-tetrahydro- (1196-87-8)

Methyl (trans-2-iodo-1-tetralin)carbamate (1210-13-5)