



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.

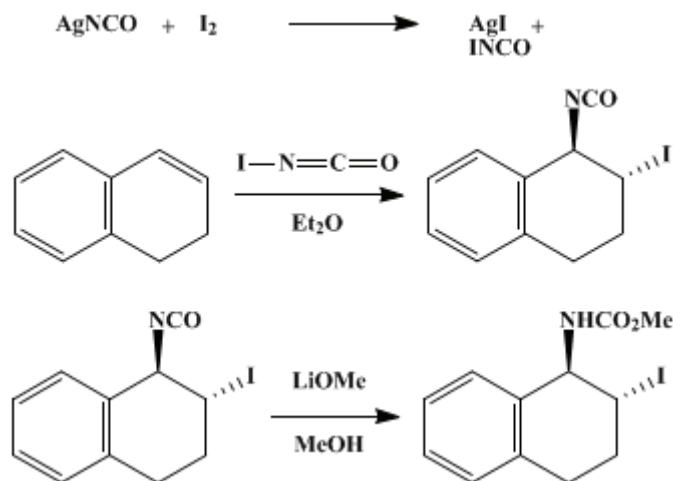
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.795 (1988); Vol. 51, p.112 (1971).

METHYL (*trans*-2-iodo-1-tetralin)CARBAMATE

[Carbamic acid, (1,2,3,4-tetrahydro-2-iodo-1-naphthalenyl)-, methyl ester, *trans*-]



Submitted by C. H. Heathcock¹ and A. Hassner².
Checked by William G. Kenyon and Richard E. Benson.

1. Procedure

A 1-l., three-necked, round-bottomed flask fitted with a mechanical stirrer, a thermometer, and a calcium chloride drying tube is immersed in an ice-salt bath and charged with 38 g. (0.25 mole) of silver cyanate (Note 1), 34.7 g. of 75% 1,2-dihydronaphthalene (0.20 mole, (Note 2)), and 400 ml. of anhydrous diethyl ether. Stirring is begun, and when the temperature of the contents of the flask has reached 0°, 50.8 g. (0.200 mole) of iodine is added in one portion. The brown mixture is stirred vigorously for 2 hours at 0–5°, then for 6 hours at room temperature. The resulting mixture, which still retains the color of iodine, is filtered through a layer of filter aid. The filtrate is transferred to a 1-l. separatory funnel and washed with 75-ml. portions of 15% sodium bisulfite solution until the ether layer is nearly colorless. The resulting ether solution is concentrated to 200 ml. using a rotary evaporator at room temperature (20 mm.).

A solution of lithium methoxide, prepared from 0.015 g. of lithium in 200 ml. of methanol, is added to the ether solution, and the resulting mixture is allowed to stand at room temperature for 1 hour. The volume is reduced to 200 ml. by distillation using a rotary evaporator at room temperature (20 mm.) before the solution is added to 600 ml. of an ice-water mixture containing 3 g. of sodium bisulfite. The solid product that separates is collected by filtration, washed with water, and air-dried. The crude carbamate (57–64 g.) is dissolved in 180 ml. of hot methanol. The resulting mixture, which is slightly cloudy, is filtered rapidly through a coarse, fluted filter paper. The filtrate is warmed to redissolve the product, and 30 ml. of water is added slowly while the solution is heated. The flask is allowed to stand overnight, then cooled to 0°. The resulting solid crystalline is collected by filtration, washed with 10 ml. of ice-cold, 4:1 (v/v) methanol–water, and air-dried, yielding 39.6–41.0 g. (60–62%) of methyl (*trans*-2-iodo-1-tetralin)carbamate, m.p. 125.5–126.5°. The IR spectrum (KBr) shows strong absorption at 3220 and 1685 cm^{-1} .

2. Notes

1. The purity of the silver cyanate used seems to be critical. Best results are obtained using product prepared in the following manner. A solution of 100 g. (0.588 mole) of silver nitrate in 3 l. of distilled water is added to a solution of 49.5 g. (0.611 mole) of potassium cyanate in 700 ml. of distilled water. The white precipitate is recovered by filtration and washed successively with distilled water, methanol,

and ether. The product is protected from light and air-dried overnight on a filter funnel attached to an aspirator. The product is then dried over phosphorus pentoxide under vacuum for at least 24 hours. 2. The submitters used technical grade dihydronaphthalene of 83% purity (Columbia Organic Chemicals Company, Inc.) or of 75% purity (Aldrich Chemical Company, Inc.) as indicated by GC. The checkers used the Aldrich product.

3. Discussion

The addition of iodine isocyanate to olefins is a general reaction leading stereospecifically to *trans*- β -iodoisocyanates, convertible to *trans*- β -iodocarbamates or ureas.³ The procedure described here is essentially that of Hassner and Heathcock.⁴ The method is applicable to unsaturated alcohols, esters, ketones, and dienes, but not to conjugated unsaturated esters or ketones. The effect of solvent on the rate of reaction for the addition of iodine isocyanate to cyclohexene has been studied;⁵ the rate of reaction in dichloromethane was found to be much greater than that in ether. Stereochemical and regiochemical effects as well as possible rearrangements during the addition have been evaluated.⁶ β -Iodocarbamates serve as useful intermediates in the synthesis of aziridines,^{4,7,8} azepines,³ 1,2-diamines,⁹ carbamates,⁶ oxazolidones,¹⁰ and amino alcohols.¹⁰

The conversion of methyl (*trans*-2-iodo-1-tetralin)carbamate to 1,2,3,4-tetrahydronaphthalene(1,2) imine is described in *Organic Syntheses*.⁸

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 967](#)

References and Notes

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Appendix

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

[methanol](#) (67-56-1)

[ether](#),
[diethyl ether](#) (60-29-7)

[Cyclohexene](#) (110-83-8)

silver nitrate (7761-88-8)

sodium bisulfite (7631-90-5)

iodine (7553-56-2)

dichloromethane (75-09-2)

potassium cyanate (590-28-3)

dihydronaphthalene,
1,2-dihydronaphthalene

lithium (7439-93-2)

silver cyanate (3315-16-0)

lithium methoxide (865-34-9)

iodine isocyanate (3607-48-5)

1,2,3,4-Tetrahydronaphthalene(1,2)imine (1196-87-8)

phosphorus pentoxide (1314-56-3)

Methyl (trans-2-iodo-1-tetralin)carbamate,
Carbamic acid, (1,2,3,4-tetrahydro-2-iodo-1-naphthalenyl)-, methyl ester, trans- (1210-13-5)