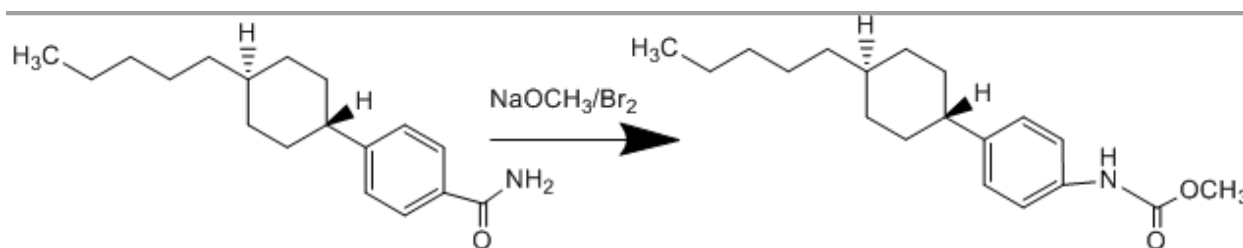


Hoffman degradation of benzamides to carbamates:

Methyl [4-(trans-4-pentylcyclohexyl)phenyl]carbamate

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Chemicals Used

4-(trans-4-Pentylcyclohexyl)benzamide,, easily prepared in high yield by basic hydrolysis of the nitrile: See Chemspider
<http://cssp.chemspider.com/Article.aspx?id=710&hw=0>

Sodium metal, pieces, 3-20mm diameter, in mineral spirits, Sigma Aldrich, 21,710-7

Methyl alcohol, 99.8%, A.C.S. reagent, Sigma Aldrich, 17,933-7

Bromine: 99.5%, A.C.S. reagent, Sigma Aldrich, 27,757-6

Procedure

A one liter 3 neck round bottom flask was equipped with mechanical stirrer, heating mantle, "Y" tube, nitrogen inlet, water condenser, internal thermometer and calcium chloride drying tube on top of the condenser. 400 ml of methanol was charged to the flask under a nitrogen blanket with stirring. With a spatula, small chunks of metallic sodium (~4g, 0.16 mole) were added over ~5 minutes through the free neck of the flask. A mild exotherm ensued to ~ 40° with gas evolution and some methanol vaporization. The free neck was stoppered and the solution allowed to cool to room temperature. Then 1.5 g (5.5 mmole) of 4-(trans-4-Pentylcyclohexyl)benzamide was added through the free neck via a powder funnel and the solution stirred until a uniform slurry was present. ~ 2ml of bromine was then pipetted into the flask and the free neck restoppered. The bromine instantly decolorized, and the amide dissolved giving a homogeneous solution with mild exotherm to ~ 45°. The mixture was warmed externally with the mantle and internal pot temperature held at ~ 40-50° for 4 hours. After removal of the mantle and allowing the solution to cool to room temperature, the solution was transferred to a one liter round bottom flask and the methanol removed on a rotary evaporator (water bath, ~ 50°, water aspirator pressure). A white residue remained to which 200

ml of water was added. The flask was manually shaken and the solid dislodged from the walls of the flask with a slightly bent spatula.

Buchner filtration of the water slurry under water aspirator pressure gave the moist product which was air dried overnight on a watch glass. 1.6g (94%) of crude carbamate resulted, which was recrystallized from the minimum amount of hot methanol, giving 1.3 g of analytically pure material.

Author's Comments

CAUTION! Sodium metal is extremely reactive with hydroxylic solvents and air. Weigh it quickly in a glove box if possible. Powdered sodium methoxide (16,499-2) or sodium methoxide in methanol,(40,306-7), both available from Sigma Aldrich, may be substituted in equimolar amounts if desired. Bromine is extremely irritating to lungs and skin. Wear latex gloves and run this reaction in an efficient fume hood.

By entirely analogous reactions other carbamates were synthesized in high yield by this procedure. See primary and secondary references.

Methyl [4-(trans-4-propylcyclohexyl)phenyl]carbamate, m.p. 127-28°.

Methyl [4-(trans-4-heptylcyclohexyl)phenyl]carbamate, m.p. 100-101°.

Data

M.p. 111-12°

I.r. (Dichloromethane) 3250, 2950, 1700, 1590 cm⁻¹

Analysis: Calculated for C₁₉ H₂₉ NO₂ : C, 75.20 H, 9.63 N, 4.62

Found: C, 75.15 H, 9.83 N, 4.67

Lead Reference

John H. MacMillan and Mortimer M. Labes, "Low Transition Temperature Liquid Crystalline Amines Incorporating the Trans-1,4-Cyclohexane Ring System", Molecular Crystals and Liquid Crystals, Vol. 55, p 61, (1979). DOI: [dx.doi.org/10.1080/00268947908069791](https://doi.org/10.1080/00268947908069791)

Other References

John H. MacMillan and Mortimer M. Labes, "Low Transition Temperature Liquid Crystalline Amines Incorporating the Biphenyl Ring System", Mol. Crystals and Liquid Crystals Letters, Vol. 56, p51, (1979). DOI: Link: <http://dx.doi.org/10.1080/01406567908071966>

John H. MacMillan and Mortimer M. Labes, "Amine Substituted Liquid Crystal Compositions", U.S. Patent 4,293,193, Oct. 6, 1981.

Chemspider deposition: <http://www.chemspider.com/Chemical-Structure.29354291.html>

Keywords: carbamate, nitrile, Hoffmann, benzamide, degradation,