Basic hydrolysis of methyl carbamates to amines:

p-(trans-4-Heptylcyclohexyl) aniline

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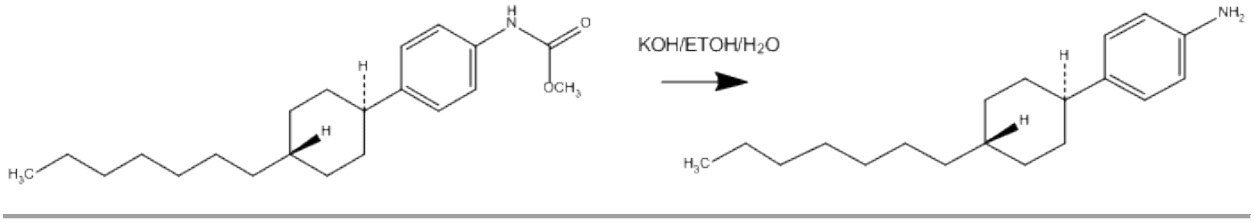

Chemicals Used:

Methyl- (p-trans-heptylcyclohexyl)carbamate, prepared in high yield from the amide by Hoffman degradation in methanol/bromine, see secondary reference 1.

Potassium hydroxide, pellets, Sigma Aldrich, 85+%, 22,147-3

Ethyl alcohol, 190 proof, Sigma Aldrich , 95+%, 49,351-1

Procedure:

To a 100ml round bottom three neck flask, equipped with heating mantle, mechanical stirrer, water condenser and nitrogen inlet was charged 33ml of 190 proof ethanol, 7 ml of deionized water and 0.512g (1.55 mmol) of

methyl- (p-trans-heptylcyclohexyl)carbamate. The mixture was stirred until homogeneous. 10g of potassium hydroxide pellets were then added and the mixture stirred until all of the pellets has dissolved. The solution was refluxed under nitrogen for 24 hours and then allowed to cool to room temperature. The reaction mixture was transferred to a 100ml round bottom flask and the ethanol removed on a rotory evaporator (water bath, bath temperature ~ 60°, water aspirator pressure). The aqueous residue was cooled to room temperature, transferred to a 100 ml separatory funnel, and extracted three times with 10ml ether portions. The combined ether extracts were dried for 2 hours over 2g anhydrous sodium sulfate and the ether solution decanted off to a 100 ml round bottom flask. The sodium sulfate residue was shaken with 10 additional ml of ether which was decanted and combined with the earlier extracts. The ether was removed on a a rotory evaporator (water bath, bath temperature ~ 60°), yielding 0.348g (88%) of essentially pure amine, which solidified on standing at room temperature.

Author's Comments:

CAUTION! Potassium hydroxide pellets are irritating and hygroscopic. Weigh quickly in a glove box if possible. Wear latex gloves.

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

p-(trans-4-propylcyclohexyl) aniline

B.p. ~ 130° (0.1 mm), m.p. 58.6°

Ir (neat film) 3420, 3350, 3250, 3050,2950,1620 cm-1.

Analysis: Calculated for $C_{15}H_{23}N$:	C,82.89	H,10.67	N,6.45
Found:	C,83.01	H,10.78	N,6.33

p-(trans-4-pentylcyclohexyl) aniline

B.p. ~ 135° (0.1 mm), m.p. 56.7°

Ir (neat film) 3500, 3420, 3350, 3250, 3050,2950,1630 cm-1.

Analysis: Calculated for $C_{17}H_{27}N$:	C,83.20	H,11.09	N,5.71
Found:	C,83.19	H,11.22	N,5.57

Data:

B.p. ~ 140° (0.1 mm), m.p. 55.8°

Ir (neat film) 3420, 3350, 3250, 3050,2950,1630 cm-1.

Analysis: Calculated for $C_{19}H_{31}N$:	C,83.45	H,11.43	N,5.12
Found:	C,83.76	H,11.18	N,5.09

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**

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.29354034.html

Keywords: carbamate, hydrolysis, Hoffmann, amine, degradation,