



SYNTHESIS OF NOVEL PRODUCTS BY USING ANILINE AND ETHYL BENZOATE

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ABSTRACT:

Simple method of Synthesis of novel products by using aniline and ethyl benzoate. This preparation was performed by using aniline and ethyl benzoate without any catalyst. This method is cheaper and less hazardous. This preparation method involves following steps purification of reactants, stirring of reaction mixture and finally products was purified by using column chromatography and identified by spectroscopic analysis. The advantage of this method is operational simplicity and avoidance of use of organic solvent and eco-friendly preparation.

KEYWORDS: aniline, ethyl benzoate, chloroform, ethanol, n-hexane, ethyl acetate, ice, water bath.

1. INTRODUCTION:

Esters are common in nature and have found widespread applications in industryⁱ. Direct amidation of esters with amines is a promising alternative synthetic method for amides. Several non-catalytic methods have been reported for the direct amidation of esters with amines that involve a large amount of promoters and suffer from low atom efficiency due to the generation of stoichiometric amounts of unwanted co-productsⁱⁱ. To overcome these problems, homogeneous catalytic methods^{iii-vii} have also been developed for the amidation of esters with amines, but the reported methods suffer from drawbacks, including limited substrate scope, high catalyst loading (>10 mol% with respect to substrate), and the need for additives. Direct synthesis of cyclic imides from dicarboxylic acids and amines by using Nb₂O₅ as a reusable Lewis acid catalyst^{viii}. Garg and co-workers recently reported nickel-catalysed direct amidation of esters with secondary aryl amines to furnish tertiary anilides^{ix}. The (O) C-N bonds in amides are essential building blocks for the discovery of pharmaceuticals, agrochemicals, and appealing chemicals^{x-xiii}. A nickel-catalysed reductive coupling method for the direct amidation of esters with nitroarenes^{xiii}.

This work provides a novel and efficient method for amide synthesis.

2. EXPERIMENTAL SECTION:

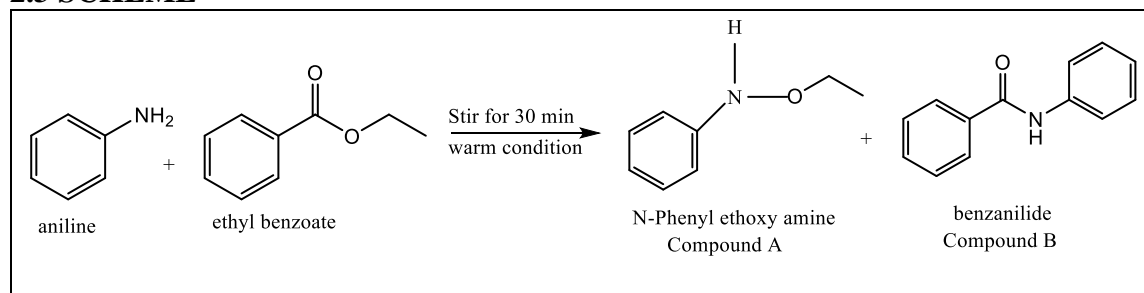
2.1 MATERIALS

Reactions were monitored by thin layer chromatography on 0.2 mm silica gel F-252 (Merck) plates. Aniline, ethyl benzoate and were obtained from Aldrich Chemical Co. And used Infrared spectral studies were carried out using Shimadzu FTIR/4000 spectrophotometer. ^1H NMR and ^{13}C NMR were recorded in $\text{CDCl}_3\text{-d}_6$ on Bruker Advance II 400 NMR spectrometer. All products were characterized by FT-IR, ^1H NMR, ^{13}C NMR and mass spectroscopy.

2.2 PREPARATION OF NOVEL PRODUCTS

To a 250ml beaker different concentrations (Table-1) of aniline and ethyl benzoate were mixed thoroughly at room temperature. Within fraction of second solid product formed. The solid product was kept into water bath at temperature ($50\text{-}60^\circ\text{C}$) and stirred for 30min. Then the solid product was crystallised out. Column chromatography was done on the product which resulted in two separate products. Then the product was confirmed by using spectral technique such as IR, ^1H NMR and ^{13}C NMR and mass spectroscopy.

2.3 SCHEME



2.4 IMAGES OF PRODUCTS



Table 1: Optimization Condition of Aniline for Reaction with Ethyl benzoate

Aniline (moles)	Ethyl benzoate (moles)	Compound (A) (%) yield	Compound (B) (%) yield
0.01	0.02	50	50
0.02	0.02	70.0	30
0.05	0.03	60	40
0.07	0.03	62.5	37.5
0.09	0.1	80	20
0.1	0.1	85	15
0.3	0.4	60	40
0.5	0.7	65	35
0.7	0.5	75	25
0.8	0.5	72	28

Table 2: Physical constant

Name of Compounds	Physical constant (°C)
N-Phenyl ethoxy amine (A)	120
Benzanilide (B)	162

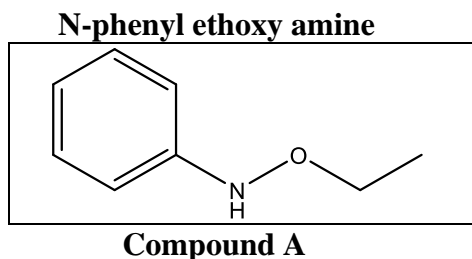
Table 3: Solubility test Compound A:

Solvent	Solubility
Water	Insoluble
Ethanol	Soluble
Acetone	Soluble
Acetic acid	Soluble
Dilute HCl	Insoluble
Water: Ethanol	Sparingly soluble

2.5. BENZANILIDE IS CONFIRMED BY FOLLOWING TEST:

5ml concentrated HCl Was added in 0.01 mole of benzanilide and stir to obtained clear solution. 5ml cooled NaNO₂ solution was added into it.

β-naphthol was added in sodium hydroxide to obtain a solution then this ice cooled 5 ml of solution was added into the previous solution dropwise and stirred well which resultant in Red/Orange dye therefore Benzanilide was confirmed.

SPECTRAL ANALYSIS:

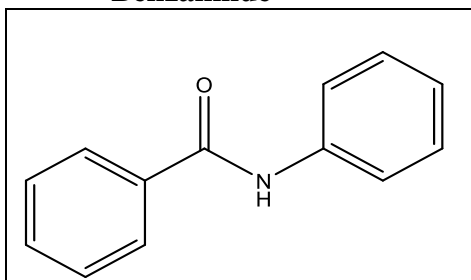
IR (KBr, cm⁻¹): 3350, 2920, 1710, 1530, 1440, 1190, 750, 690.

¹H-NMR (CDCl₃-d₆) (δ ppm): 1(t), 1.3(t), 4.4(q), 5(s), 7-7.7(m).

¹³C-NMR (CDCl₃-d₆) (δ ppm): 14, 22, 24, 30, 62, 122,125, 128, 130,132, 140, 174,178.

Mass (m/z values): 102.1, 262.1, 284.1, 316.2.

Benzanilide



Compound B

IR (KBr, cm^{-1}): 3350, 2910, 1710, 1600, 1180, 1130, 1080, 470

^1H NMR ($\text{CDCl}_3\text{-d}_6$) (δ ppm): 1(m), 3.2, 3.4, 5(s), 7(m), 7.2(t), 7.5(t).

^{13}C -NMR ($\text{CDCl}_3\text{-d}_6$) (δ ppm): 22, 26, 30, 42, 122, 126, 130, 140, 176.

Mass (m/z values): 94.1, 262.1, 284.1, 300.1, 316.2

3. RESULT AND DISCUSSION:

It was observed that Synthesis of N-Phenyl ethoxy amine (A) and benzanilide (B) by using 0.1 mole of aniline and 0.1 mole of ethyl benzoate. In this product A that is to N-Phenyl ethoxy amine (major) gives maximum yield as compared to Benzanilide (minor). Products A and B confirmed by spectral data. This method for preparation of compound A as a novel product. This product is further confirmed by using spectral data.

4. CONCLUSION:

We have mentioned a novel method for the preparation of benzanilide and N-Phenyl ethoxy amine from aniline and ethyl benzoate without any catalyst.

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