

# Preparation of n n- diethyl-m-toluamide (deet) essay



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Preparation of N, N-Diethyl-m-toluamide (DEET) and its Identification by IR and NMR Spectroscopy Eim A. Chemist CHEM 304 July 10, 2005

INTRODUCTION N, N-Diethyl-m-toluamide (DEET) is the active ingredient in many insect repellants. 1 In this experiment, DEET will be prepared from m-toluic acid through the intermediate acid chloride and then identified by its IR and proton NMR spectra. The overall reaction is a series of two acyl substitutions and is shown in Scheme 1 below: [pic] Scheme 1

Carboxylic acids can be converted to acid chlorides by treatment with a compound such as phosphorus trichloride (PCl<sub>3</sub>) or thionyl chloride (SOCl<sub>2</sub>). 2 The reactive acid chloride can then be treated with a primary or secondary amine to give the amide along with HCl, which reacts with the excess amine to give an alkylammonium chloride salt. The mechanism of this process is shown on the following page in Scheme 22: [pic] Scheme 2 To carry out this reaction, the apparatus shown in Figure 1 will be assembled. The apparatus must be dry, since thionyl chloride will react with water to give sulfur dioxide and hydrogen chloride. [pic] Figure 13 m-Toluic acid and thionyl chloride will be charged into the reaction flask (USE A HOOD! ), then boiled gently to effect the formation of the acid chloride. The acid chloride will then be cooled to room temperature and dissolved in anhydrous ether. Ice-cold diethylamine will be added as a solution in anhydrous ether to form the amide. The resulting ether mixture will be washed with aqueous sodium hydroxide (to remove any excess acid chloride), then washed with hydrochloric acid (to remove any excess diethylamine).

The resulting ether solution of DEET will be dried and evaporated to yield the crude product, which will then be purified by column chromatography to

afford pure DEET. The percent yield from m-toluic acid will be determined and the product will be analyzed by transmission infrared spectroscopy (IR) as a neat sample using NaCl plates<sup>5</sup> to confirm its structure by (1) looking at the major absorptions and comparing them to a correlation table<sup>6</sup> and (2) by comparing the spectrum to that of an authentic sample. The major IR absorption is expected to be the amide carbonyl at 1640 - 1700 cm<sup>-1</sup>. The product will also be analyzed by <sup>1</sup>H-NMR spectroscopy as a solution in CDCl<sub>3</sub>. The <sup>1</sup>H-NMR chemical shifts are expected to be a multiplet at  $\delta$  7 - 8 for the four aromatic protons, a singlet around  $\delta$  2 - 3 for the three protons on the benzylic methyl group, a quartet at  $\delta$  2 - 3 for the four CH<sub>2</sub> protons in the ethyl groups, and a triplet at around  $\delta$  0.5 - 1 for the six CH<sub>3</sub> protons in the ethyl groups. <sup>7</sup> Table of Chemical Substances<sup>8</sup> | Reagent |

Structure/Formula	Role	Mol. Wt.	Mp		m-Toluic acid	No	No	No	No	
Thionyl chloride	Yes (Inhalation, rat: LC50 =				Yes	No	No			500
ppm/ <sup>1</sup> H)					Diethylamine	No	Yes	Yes (Fp:28 oC	No	
					Diethyl ether	No	No	Yes (Fp:-45 oC	No	
					Sodium hydroxide, 10% aq	No	Yes	No	No	
					Hydrochloric acid, 10%	No	Yes			
					Sodium sulfate	No	No	No	No	
					N, N-Diethyl-m-toluamide	No				
					Alumina	No	No	No	No	
					Hexane	No	No	Yes (Fp: -15		
						No				

Note: Fp is the abbreviation for Flash Point

Techniques: Thionyl chloride is toxic and corrosive! Do not breath the vapors! Use in a hood! When heating a reaction apparatus, be sure that it is open to the air so that pressure build up and subsequent rupture of the apparatus does not occur. When heating liquids, make sure the liquid is stirred (or a boiling chip is added) to prevent " bumping". When performing an extraction, make sure to vent the separatory funnel often to prevent

pressure build-up. EXPERIMENTAL The apparatus shown in Figure 1 was assembled.

The 10-mL reaction flask was charged with 0.275 g of m-toluic acid (0.0020 mol) and 0.30 mL of thionyl chloride (0.492 g, 0.0041 mol). The condenser water was started, and the mixture was gently heated with stirring on an aluminum block (block temp ~ 90 °C) until boiling started. The reaction mixture was then gently boiled for about 15 minutes. After the boiling period was finished, the reaction mixture was cooled to room temperature. 4.0 mL of anhydrous ether were added, and the mixture was stirred at room temperature until a homogeneous mixture was obtained. To this solution was added (dropwise over a 15 minute period) a solution of 0.6 mL of cold (0 °C) diethylamine (0.462 g, 0.0063 mol) in 1.33 mL of anhydrous ether. During the addition, a thick white cloud of diethylamine hydrochloride was formed. After complete addition, the reaction mixture was stirred at room temperature for about 10 minutes. 10% aqueous sodium hydroxide (2 mL) was then added, and the reaction mixture was stirred for an additional 15 minutes at room temperature, then poured into a separatory funnel and allowed to separate. The aqueous layer was discarded, and the organic layer was washed with an additional portion of 10% aqueous sodium hydroxide (2 mL), followed by a portion of 10% hydrochloric acid (2 mL).

The organic layer was washed with water (2 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to yield crude N, N-diethyl-m-toluamide as dark brown liquid. The crude product was filtered through a short alumina column using hexane as the eluent (~ 5 mL). The hexane solution was evaporated to give 0.340 g of pure N, N-diethyl-m-toluamide as a yellow liquid. RESULTS AND DISCUSSION

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Reaction of m-toluic acid with thionyl chloride, followed by diethylamine produced 0.340 g of a yellow liquid the IR spectrum of which unequivocally showed the presence of the amide carbonyl functional group at 1633  $\text{cm}^{-1}$ . In addition, absorptions due to aliphatic C-H (2980 - 2880  $\text{cm}^{-1}$ ), and aromatic C=C (at 1585  $\text{cm}^{-1}$ ). The IR spectrum is attached to this report.

These data are consistent with the structure of N, N-diethyl-m-toluamide (DEET), shown in Figure 2 below: [pic] Figure 2: N, N-Diethyl-m-toluamide (DEET) In addition, the IR of the product closely corresponds with that of an authentic sample of N, N-diethyl-m-toluamide (DEET) shown in the lab text. 9 Also, the  $^1\text{H-NMR}$  shows the presence of four (4) aromatic protons in the region 7.3 - 7.1 ppm, as well as a three (3) proton singlet at 2.35 ppm, which corresponds to the benzylic methyl group. The presence of two ethyl groups is clearly shown by the presence of two quartets which integrate to 2 protons each at 3.53 and 3.24 ppm, and two triplets which integrate to 3 protons each at 1.23 and 1.09 ppm.

Although the ethyl groups look chemically equivalent, because of restricted rotation about the C-N bond (due to the relatively large contribution of the resonance structure shown in Figure 3 to the overall structure of the DEET molecule), they are not equivalent, and this is reflected in the  $^1\text{H-NMR}$ , which contains signals for two chemically nonequivalent ethyl groups. [pic] Figure 3. Alternative Resonance Structure of DEET Furthermore, the  $^1\text{H-NMR}$  of the product isolated from this experiment closely corresponds to that of an authentic sample of DEET. 10 It can therefore be concluded that the product synthesized in this laboratory was, in fact, DEET. 0.34 g of N, N-diethyl-m-toluamide (DEET) was produced from 0.275 g of m-toluic acid.

This corresponds to a percent yield of 88. 1%. The calculations are shown below: The limiting reactant in this preparation is m-toluic acid. Therefore, the theoretical yield of DEET is calculated as follows: 1 mol DEET193. 1 g DEET

Theoretical yield of DEET = (moles m-toluic acid) x  $\frac{1 \text{ mol DEET}}{1 \text{ mol m-toluic acid}}$  x  $\frac{193.1 \text{ g DEET}}{1 \text{ mol DEET}}$

Theoretical yield of DEET = (0. 0020 mol) x  $\frac{1 \text{ mol DEET}}{1 \text{ mol m-toluic acid}}$  x  $\frac{193.1 \text{ g DEET}}{1 \text{ mol DEET}}$   
 = 0. 386 g DEET  
 Actual yield of DEET (0. 340 g)  
 % Yield =  $\frac{0.340 \text{ g}}{0.386 \text{ g}} \times 100 = 88.1\%$  Theoretical

Yield of DEET (0. 386 g) The experiment proceeded as planned, giving a very good yield (88. 1%) of DEET. There were no spills or other abnormal physical losses, so it is doubtful that this procedure can be improved much further without a significant amount of effort. SUMMARY AND CONCLUSIONS

In this experiment, it was shown that N, N-diethyl-m-toluamide (DEET) could be produced from m-toluic acid by treatment with thionyl chloride followed by reaction of the intermediate acid chloride with diethylamine in an overall yield of 88. 1%. That the product synthesized was, in fact, N, N-diethyl-m-toluamide was demonstrated by its IR and 1H-NMR spectra. REFERENCES 1.

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ANSWERS TO

QUESTIONS 1. Why is the reaction mixture extracted with 10% aqueous sodium hydroxide? Write an equation. In the event any acid chloride did not react with diethylamine, the sodium hydroxide converts the residual acid chloride to the sodium salt of m-toluic acid. This salt is water soluble and is extracted out of the organic layer into the aqueous layer and therefore is separated from the product. The equation which describes this process is:

[pic] 2. What reaction would take place if the acid chloride of m-toluic acid were mixed with water? Write an equation.

The acid chloride would hydrolyze according to the following equation: [pic]

NOTE: The in-lab write up from your lab notebook is to be included here (example notebook entry is contained in the example lab report " Isolation of Eugenol from Cloves by Steam Distillation and its Identification by Infrared Spectroscopy" [pic] Reproduced from the Spectral Database for Organic Compounds (SDBS). [www.aist.go.jp/RIODB/SDBS/cgi-bin/cre\\_index.cgi](http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi) (accessed May, 2006) [pic] | | | Assign. Shift(ppm) | | | A 7. 51 | | B 7. 18 | | C 7. 139 | | E \*1 3. 53 | | F \*1 3. 24 | | G 2. 352 | | J \*2 1. 23 | | K \*2 1. 09 | | Reproduced from the Spectral Database for Organic Compounds (SDBS). [www.aist.go.jp/RIODB/SDBS/cgi-bin/cre\\_index.cgi](http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi) (accessed May, 2006)