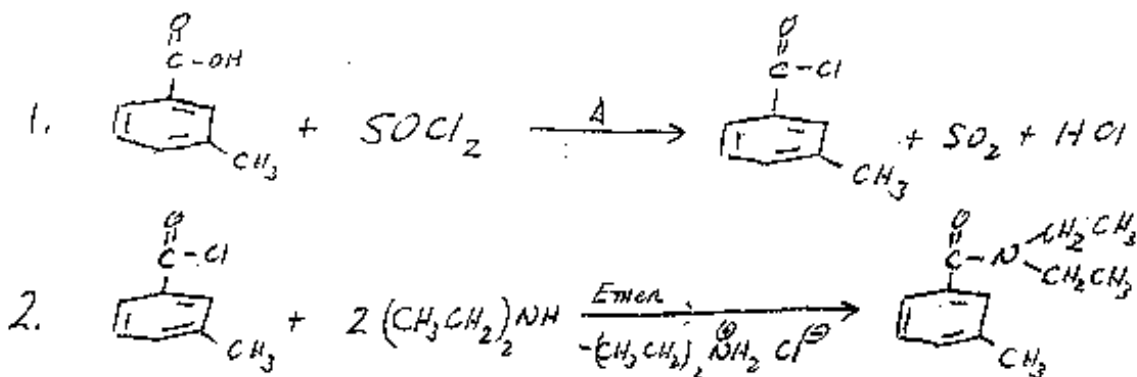


DATE	EXP. NUMBER	EXPERIMENT	
8/28/2012	EAC-14	Preparation of DEET	
NAME		LAB PARTNER	WITNESS
Eim A. Chemist			

Purpose: To prepare *N,N*-diethyl-*m*-toluamide (DEET) and characterize it by IR and proton NMR

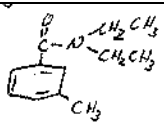
Reaction:



Physical Data and Safety:

Reagent	Structure/Formula	Mol. Wt.	Mp	Bp	Density	Safety
<i>m</i> -Toluic Acid	 $\text{C}_8\text{H}_8\text{O}_2$	136.15	108 -112 °C	236 °C	1.05 g/mL	Causes eye, skin, respiratory tract irritation
Thionyl Chloride	SOCl_2	118.97	-105 °C	76 °C	1.63 g/mL	May be fatal if inhaled. Causes burns by all exposure routes. Water-reactive. Contact with water liberates toxic gas. Lachrymator (substance which increases the flow of tears).
Sodium Sulfate	Na_2SO_4	—	—	—	—	Possible irritant
Diethylamine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	73.13	-50 °C	55 °C	0.7 g/mL	Harmful if absorbed through the skin. Causes eye and skin burns. Causes digestive and respiratory tract burns. Extremely flammable liquid and vapor. Vapor may cause flash fire.
Diethyl Ether	$(\text{CH}_3\text{CH}_2)_2\text{O}$	74.12	-116 °C	35 °C	0.7 g/mL	Extremely flammable liquid and vapor. May form explosive peroxides. Irritating to eyes, skin and respiratory tract. Vapors may cause drowsiness and dizziness.
Sodium Hydroxide, 10% aq.	NaOH	—	—	—	—	Corrosive. Causes eye and skin burns. May cause respiratory tract burns.

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Reagent	Structure/Formula	Mol. Wt.	Mp	Bp	Density	Safety
Hydrochloric Acid, 10%	HCl	—	—	—	—	Causes eye, skin, and respiratory tract burns. Corrosive.
N,N-Diethyl-m-toluamide	 $C_{12}H_{17}NO$	191.27	—	111 °C	0.996 g/mL	Irritant
Alumina	Al ₂ O ₃	—	—	—	—	May cause respiratory tract irritation. May cause lung damage. May cause mechanical eye and skin irritation.
Hexane	C ₆ H ₁₄	86.18	-95 °C	62 - 69 °C	0.678 g/mL	Flammable liquid and vapor. Harmful by inhalation, in contact with skin and if swallowed. Irritating to eyes and skin. Vapors may cause drowsiness and dizziness.

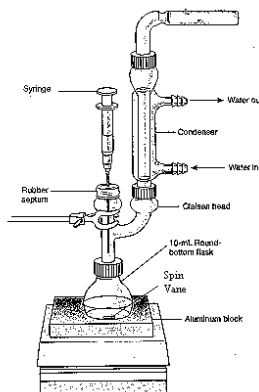
When heating a reaction apparatus, be sure that it is open to the air so that pressure build up and subsequent rupture of the apparatus does not occur.

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.

Procedure

1. Assemble the apparatus sketched below, be sure to vent the outlet into the hood! (NOTE: Apparatus must be dry!)



2. Add 0.272 g m-toluic acid to the reaction flask.

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3. In a HOOD(!), add 0.30 mL of thionyl chloride.
4. Start circulation of water through the reflux condenser, then heat the reaction gently until the mixture begins to boil.
5. Reflux the mixture gently for 15 min, then cool to room temperature.
6. Using the syringe, add 4.0 mL anhydrous ether to the mixture and stir until solution is obtained.
7. Dissolve 0.66 mL of ice-cold diethylamine in 1.33 mL of anhydrous diethyl ether
8. Add solution from step #7 via syringe to the reaction flask dropwise over 10 - 15 min.
9. Stir reaction mixture for 10 min at room temperature.
10. Add 2 mL 10% NaOH (via syringe) and stir reaction mixture for 15 min at room temperature.
11. Transfer to separatory funnel and discard aqueous (bottom) layer.
12. Wash organic layer with 2 mL 10% NaOH. Discard aqueous (bottom) layer.
13. Wash organic layer with 2 mL 10% HCl. Discard aqueous (bottom) layer.
14. Dry the organic layer with sodium sulfate, then decant to a small conical vial.
15. Evaporate ether using a hot plate on a low setting.
16. Filter the crude product from step 15 through 1.0 g alumina in Pasteur pipet column, elute with hexane (5 - 7 mL) into a small tared beaker.
17. Evaporate the hexane on a hot plate over low heat.
18. Weigh product, obtain IR and proton NMR spectra.

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Data and Observations

<u>Step</u>	<u>Data/Observations/Calculations</u>
2.	Wt of m-toluic acid: 0.275 g. $0.275 \text{ g} (1 \text{ mol}/136.15 \text{ g}) = 0.0020 \text{ mol}$
3.	Vol $\text{SOCl}_2 = 0.30 \text{ mL}$. $0.30 \text{ mL} (1.63 \text{ g}/1 \text{ mL}) = 0.489 \text{ g}$. $0.489 \text{ g} (1 \text{ mol}/118.97 \text{ g}) = 0.0041 \text{ mol}$
5.	Refluxed 20 min, rxn took about 10 min to cool to room temperature.
6.	4.3 mL ether added, solution was a brown color
7.	Vol diethylamine = 0.70 mL. $0.70 \text{ mL} (0.7 \text{ g}/1 \text{ mL}) = 0.49 \text{ g}$ $0.49 \text{ g} (1 \text{ mol}/73.13 \text{ g}) = 0.0067 \text{ mol}$ Vol ether used = 1.5 mL
8.	During the addition, a thick white cloud formed over the reaction mixture.
10.	Vol 10% NaOH = 2.4 mL
12, 13	Vol 10% NaOH = 2 mL, vol 10% HCl = 2 mL
14.	Enough sodium sulfate was added so that free-flowing granules were present, solution allowed to stand over sodium sulfate for about 15 min.
15.	Hot plate setting = 3, slow stream of air was directed over the top of the vial to assist evaporation. Crude product was a dark-brown liquid.
16.	Alumina removed the brown color from the product.
17.	Hot plate setting = 3, slow stream of air was directed over the top of the vial to assist evaporation. Product was a yellow liquid

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18. Beaker tare wt = 31.873 g
 Beaker + DEET = 32.213 g
 Wt DEET = 0.340 g (pale yellow oil).

Theoretical yield calculation:

Limiting reagent is *m*-toluic acid (MTA, 0.0020 mol)

$$0.0020 \text{ mol MTA} (1 \text{ mol DEET} / 1 \text{ mol MTA}) (191.27 \text{ g DEET} / 1 \text{ mol DEET}) = 0.383 \text{ g DEET}$$

$$\text{Percentage yield} = (0.340 \text{ g} / 0.383 \text{ g}) \times 100 = 88.8\%$$

FTIR (film, NaCl plates): 2980, 2880 (sp^3 C-H), 1633 (C=O), 1585 (aromatic C=C) cm^{-1}
 IR corresponds to that of an authentic sample (see Spectral Database for Organic Compounds)

1H -NMR ($CDCl_3$): δ 7.3 - 7.1 (m, 4H, Ar-H), 3.53 (q, 2H, ethyl CH_2), 3.24 (q, 2H, ethyl CH_2), 2.35 (s, 3H, Ar- CH_3), 1.23 (t, 3H, ethyl CH_3), 1.09 (t, 3H, ethyl CH_3)
 NMR corresponds closely to that of an authentic sample (see SDBS)

Conclusions

DEET could be produced in 88.8% yield from *m*-toluic acid, and the identity was confirmed by IR and proton NMR