Preparation of Methyl 3-Nitrobenzoate
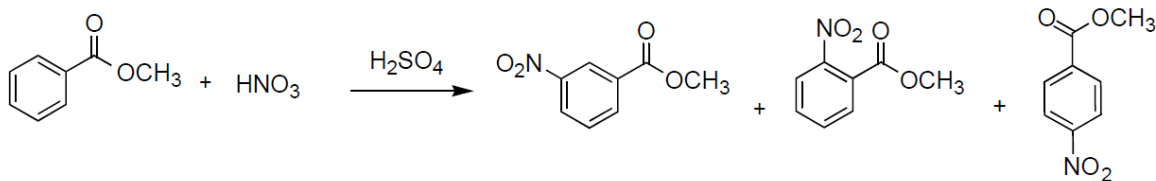
Form	$C_8H_8O_2$	HNO_3	H_2SO_4	$C_8H_7NO_4$		
M. Wt.	136.15	63.01	98.08	181.14		
mL	.210	.16	1.0	Th. Yld. = .00169 moles		
conc	100%	70%	98%	= .306 g		
dens	1.094 g/mL	1.42 g/mL	1.84 g/mL			
gms	.230	.159	1.84	69%	28%	3%
moles	.00169	.0025	.019			

To a 3 mL reaction vial containing a spin vane was added methyl benzoate (0.210 mL, 0.230 g, 0.00169 moles) and conc. sulfuric acid (1.0 mL, 1.84 g, 0.019 moles). The reaction vial was capped with a condenser. *[Note: the purpose of the condenser is solely to aid in clamping the reaction flask in the ice bath.]* The reaction flask is subsequently cooled in an ice bath for **5 minutes**, then the conc. (70%) nitric acid (.16 mL, .159 g HNO_3^-, 0.0025 moles) is added dropwise to the cold, stirred reaction mixture over 30 – 40 seconds. *[Note: too rapid an addition increases the amount of byproducts; too slow of an addition will result in incomplete nitration. The addition is best accomplished using a 9 inch disposable pipette and adding through the top of the condenser. The tip of the pipette should be just above the surface of the reaction mixture during the addition. 12 drops of conc.$HNO_3 \approx 0.16g$].* Immediately after the addition is complete, the ice bath is removed, and the reaction mixture is stirred at room temperature for 10 minutes. The reaction mixture is then poured into 5 g of ice. The resulting mixture is scratched and stirred with a glass stir rod until the oily product solidifies. The solid product is vacuum filtered via a Hirsh funnel. The solid is washed with cold water (2 x 2 mL), then with ice-cold methanol (2 X .5 mL). *[Note: thin layer chromatography (silica gel, 8:2 hexane / ethyl acetate) shows that the crude solid is a mixture of at least 3 products in major, minor and trace amounts. In runs where the too little sulfuric acid is added, TLC also shows the presence of starting methyl benzoate. When this happens, the product often fails to solidify when added to the ice.)* The crude, partially dried product is recrystallized from methanol (Craig tube) to give the pure methyl 3-nitrobenzoate as a white solid (0.162 g, 53%): mp = 75-77 ^{O}C; IR 1725 (C=O), 1530, 1350 (NO2) and 1280 (C-O) cm^{-1}. TLC (silica gel, 8:2 hexane/ethyl acetate) showed the recrystallized product to consist of a single material, Rf = 0.35.