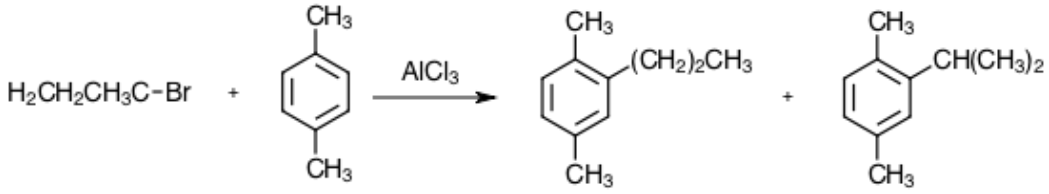
Friedel-Crafts Alkylation

Summary:

The Friedel-Crafts alkylation reaction proceeds similarly to the acylation reaction, but uses an alkyl halide to attach an alkyl group to an aromatic ring. Anhydrous aluminum chloride is used in this classic example and is extremely hygroscopic and reacts rapidly with water to produce hydrogen chloride fumes.



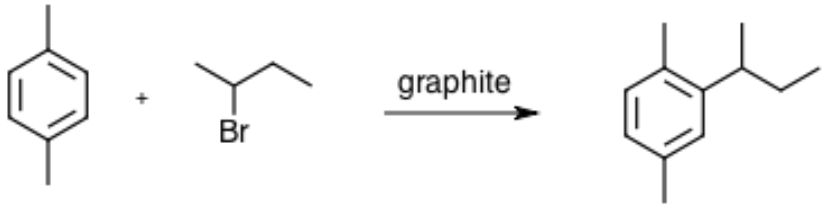
Reference: Friedel-Crafts Alkylation of p-xylene, Experimental Organic Chemistry, Gilbert & Martin, 5th edition, 2011, p. 495-496.

Chemical Name Aldrich Catalog #	Amount per 100 students (g or mL)	EH&S	Purchasing cost per 100 students ($)
p-xylene 134449	750 mL		$47.81
Aluminum chloride, anhydrous 237051	35 g		$7.39
1-bromopropane B78106	425 mL		$59.50
Crushed ice n/a	500 g		n/a
Sodium sulfate, anhydrous 239313	250 g		$17.50

Friedel-Crafts Alkylation – A Greener Approach

Summary:

This alternative Friedel-Crafts Alkylation reaction uses a graphite to catalyze the alkylation of p-xylene by 1-bromobutane. This procedure eliminates the use of aluminum chloride and the associated aqueous work-up of the product.



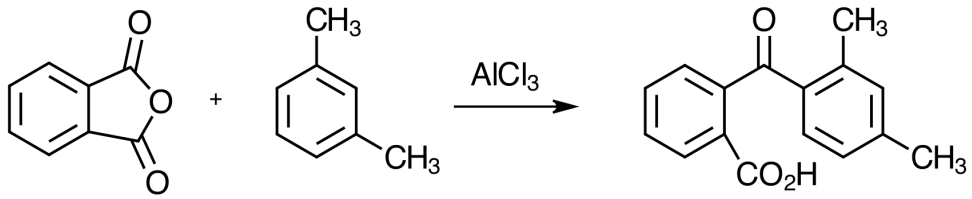
Reference: A Greener Alternative to Aluminum Chloride Alkylation of Xylene, Sereda, G.A. And Rajpara, V.B., J. Chem. Ed., 2007, 84(4), 692

Chemical Name Aldrich Catalog #	Amount per 100 students (g or mL)	EH&S	Purchasing cost per 100 students ($)
p-xylene 134449	250 mL		$24.38
2-bromobutane B59500	22 mL		$7.26
Graphite (<20 micron particles) 282863	25 g		$1.56
Heptane 246654	750 mL	*	$37.13

Friedel-Crafts Acylation

Summary:

The Friedel-Crafts reaction is a classic electrophilic aromatic substitution reaction that typically uses anhydrous aluminum chloride, a strong Lewis acid, to produce acylonium ions, which function as electrophiles in the reaction. Anhydrous aluminum chloride is extremely hygroscopic and reacts rapidly with water to produce hydrogen chloride fumes.



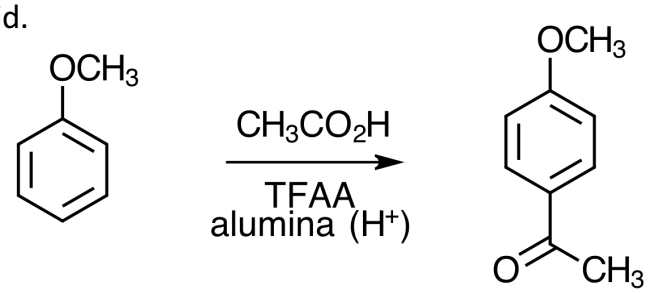
Reference: Friedel-Crafts Acylation of m-Xylene with Phthalic Anhydride, Experimental Organic Chemistry, Gilbert and Martin, 5th Edition, 2011, p. 505-506.

Chemical Name Aldrich Catalog #	Amount per 100 students (g or mL)	EH&S	Purchasing cost per 100 students ($)
Phthalic anhydride 320064	50 g		$5.41
Aluminum chloride, anhydrous 237051	100 g		$21.12
m-xylene 185566	300 mL		$28.31
Hydrochloric acid, conc. 320331	100 mL	*	$3.90
Water n/a	500 mL		n/a
Diethyl ether 346136	1400 mL	*	$128.38
Hydrochloric acid, 6M 320331	250 mL		$4.88
Sodium sulfate 239313	500 g		$35.00
Ethanol, 50% 459836	500 mL		$19.38

Friedel-Crafts Acylation – A Greener Approach

Summary:

This greener approach to a Friedel-Crafts acylation avoids the use of aluminum chloride by using an activated alumina catalyst and trifluoroacetic anhydride. The solvent-less reaction is the first step in a 2-step synthesis of p-anisic acid.



Reference: Introducing environmentally benign synthesis into the introductory organic lab - a greener Friedel-Crafts acylation, The Chemical Educator. 2001, 6(1), 25–27

Chemical Name Aldrich Catalog #	Amount per 100 students (g or mL)	EH&S	Purchasing cost per 100 students ($)
Anisole 123226	16.5 mL		$2.13
Activated acidic aluminum oxide (Brockmann 1) 199966	150 g		$14.37
Trifluoroacetic anydride 106232	62.5 mL	*C	$58.74
Glacial acetic acid 695092	17.5 mL		$1.20
Diethyl ether 346136	1500 mL	*F	$127.00
Sodium bicarbonate, sat. solution S6014	1500 mL		$9.79
Brine solution 746398	1500 mL		$34.28
Sodium sulfate, anhyd. 239313	250 g		$17.50

Comparison: Friedel-Crafts

Comparison of Friedel-Crafts Acylation:

- Greener method avoids the use of aluminum chloride, which is highly reactive to moisture, producing hydrogen chloride fumes
- Both methods utilize diethyl ether as a solvent in the work-up procedures, which is highly flammable
- Greener method can be used as part of a multi-step synthesis as product can be used to create p-anisic acid in a second reaction
- Greener method avoids the use of concentrated hydrochloric acid

	Purchasing costs	Waste (per 100 students)	"Greener" benefits
Greener method	$265.01	4.6 L liquid waste (3L aqueous waste) 500 g solid waste	
Traditional method	$246.38	3.2 L liquid waste 250 g solid waste	

Comparison of Friedel-Crafts Alkylation:

- Greener method eliminates the use of aluminum chloride, which is extremely hygroscopic and reacts rapidly with water to produce hydrogen chloride fumes
- Greener method uses a graphite catalyst which can be re-used to reduce waste

	Purchasing costs	Waste (per 100 students)	"Greener" benefits
Greener method	$94.71	1 L liquid waste	
Traditional method	$132.20	1.7 L liquid waste 250 g solid waste	

Other greener lab options to explore:

- A Research-Based Undergraduate Organic Laboratory Project: Investigation of a One-Pot, Multicomponent, Environmentally Friendly Prins–Friedel–Crafts-Type Reaction, J. Chem. Educ. 2012, 89, 265-267
- A Microwave-Assisted Friedel–Crafts Acylation of Toluene with Anhydrides, J. Chem. Educ., 2013, 90 (3), pp 390–392
- The Friedel-Crafts reaction: Acetylation of Ferrocene, Doxsee, K. M., Hutchison, J.E., Green Organic Chemistry – Strategies, Tools, and Laboratory Experiments, Print 2004, pp. 225-230.