

THE FRIEDEL AND CRAFTS REACTION IN QUALITATIVE
ORGANIC CHEMISTRY. I. AROYL PROPIONIC ACIDS OF
AROMATIC ETHERS

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The reaction of phthalic anhydride and aluminum chloride with aromatic hydrocarbons was applied to qualitative organic chemistry by Underwood and Walsh (1). The suggestion was made by these experimentors that this reaction could be extended to aryl halides. An excellent summary of the "Friedel and Crafts Reaction with Aliphatic Dibasic Anhydrides" by Berliner (2) indicates the yields to be good with succinic anhydride and aryl ethers on a macro scale. The reduction of this reaction to a small scale would provide a derivative in addition to the sulfonamides.

A procedure which is a modification of that suggested by Berliner (2) has been developed. The reaction is run at room temperature with mechanical stirring. While the acids that are obtained are not as pure as those from the low-temperature reaction that is allowed to stand for three days in an ice-chest, their purity is fairly good as judged by the number of recrystallizations needed, and the yields are fairly high. While the steam-distillation which is required to remove the solvent has been shown responsible for the hydrolysis of some phenolic ethers, this does not seem to have occurred, for the observed neutral equivalents of the acids are in good agreement with the calculated values (see Table I). The melting points of most of the acids are high, and the melting point spread is large enough to readily identify the aryl ethers from which these acids are derived.

The procedure was successful with 20 ethers. The method failed with safrole due to no yield; with *m*-cresyl ethyl, *o*-methoxy diphenyl, β -naphthyl ethyl, and β -naphthyl methyl ethers due to low purity of product; with *p*-ethoxy diphenyl ether due to insolubility of the sodium salt; with *p*-bromoanisole due to low yield. The β -naphthyl ethers may be succinoylated under other conditions (2).

The neutral equivalent has been determined to obtain the molecular weight of the acid. No attempt has been made to assign structures to the acids which have not been previously prepared.

EXPERIMENTAL

Apparatus. A synchronous motor of 200 or 300 rpm may be used with a propellor type stirrer to insure adequate mixing and to aid in the evolution of HCl. The rubber stopper which carries the glass bearing for the stirrer is notched to permit the escape of the HCl.

Procedure. The molar ratio of the ether:anhydride:aluminum chloride used is 1:1:2. The weight of ether taken is one gram, and this determines the other weights. Care must be taken to maintain anhydrous conditions—the precautions suggested by Fieser (3) should be followed.

Succinic anhydride is weighed into a 25 × 150 mm. test tube and is dissolved by heating

with 20 ml. of a solvent which consists of 16 ml. of *sym*-tetrachloroethane and 4 ml. of nitrobenzene. The solution is cooled to room temperature and anhydrous powdered AlCl_3 is added; it dissolves almost completely with the evolution of heat. The test tube is again cooled to room temperature, and one gram of the ether is added from a medicine dropper over a period of 20-30 minutes. Solid ethers are added portionwise over a period of 5 minutes.

TABLE I
AROYL PROPIONIC ACIDS OF AROMATIC ETHERS

ETHER USED ^d	B.P., ^e °C.	DERIVATIVE M.P., °C. ^a Found	TIMES RECRYSTAL- LIZED	CRUDE YIELD, %	NEUTRAL EQUIV.		LITERATURE M.P., °C.
					Obsv'd	Calc'd	
Anisole	154	148-150	2×	75	208.2	208.8	147 (5)
Phenetole	172	137-139	2×	82	222.1	222.3	137-138 (6)
<i>p</i> -Cresyl methyl ether	176	107-108	3×	65	222.9	222.3	115-117 (8)
<i>m</i> -Cresyl methyl ether	177	135-137.5	2×	75	223.0	222.3	138 (8)
<i>o</i> -Cresyl ethyl ether	192	172-173	3×	79	237.5	236.3	172-173 (7)
<i>p</i> -Cresyl ethyl ether	192	139-141	2×	52	237.0	236.3	140 (7)
<i>p</i> -Chloroanisole	200	119-121	2×	25	243.7	242.7	
Veratrole	206	163-164	2×	60	238.4	238.2	160-161 (9)
<i>o</i> -Chlorophenetole	208	190-191.5	2×	79	258.0	256.7	184 (10)
<i>n</i> -Butyl phenyl ether	210	110-112	2×	72	250.2	250.3	112 (6)
<i>p</i> -Chlorophenetole	212	156-158	4×	20	252.0	256.7	
Resorcinol dimethyl ether	214	150-151.5	2×	49	239.5	238.2	148 (11)
<i>o</i> -Bromoanisole	218	189.5-191.5	2×	59	288.2	287.1	
<i>o</i> -Bromophenetole	224	201-202	1×	86	302.2	301.1	
Resorcinol diethyl ether	235	148.5-150.5	2×	65	267.0	266.3	
Phenyl ether	252	119-120	2×	94	271.4	270.3	117 (14)
Ethyl α -naphthyl ether	278	202-203	2×	82	271.2	272.3	198 (13)
Hydroquinone diethyl ether	72 ^c	148-150	2×	57	267.2	266.3	147.4-148.5 (12)
<i>p</i> -Bromophenyl phenyl ether	305 (15)	161.5-162.5	2×	82	349.3	348.4	
Resorcinol dibutyl ether	290 ^b	118-119	2×	69	323.6	322.4	

^a All melting points taken with a calibrated thermometer. ^b This boiling point experimentally determined. ^c Melting point. ^d The other ethers upon which the reaction was tried but which did not yield a satisfactory derivative were: *p*-ethoxyl diphenyl, β -naphthyl ethyl ether, *o*-methoxy diphenyl, β -naphthyl methyl ether, *m*-cresyl ethyl ether, safrole, and *p*-bromoanisole. ^e The melting and boiling points of the ethers were taken from Shriner and Fuson. (4)

Stirring is continued for a total of 2½-3 hours. At this point the color is generally dark red. The reaction mixture is then poured into a 200-ml. round-bottom flask which contains one ice cube and 10 ml. of 6 N HCl. Water is added and the contents of the flask are boiled until the solvent is removed. The flask is then cooled and the solid is removed. The solid is then returned to the flask, and is dissolved by heating with 10 ml. of 10% sodium carbonate. The solution is treated with a small amount of charcoal and is then filtered. The cold

filtrate is carefully acidified with 6 N HCl. After the acidified solution is allowed to stand a few minutes, the solid is filtered. The solid acid may be recrystallized from ethanol or dilute ethanol.

The acids are dried in a vacuum desiccator over Drierite.

The *neutral equivalents* are taken by dissolving the acid in 50 ml. of hot alcohol and titrating with aqueous 0.12 N NaOH with phenolphthalein as the indicator.

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SUMMARY

The Friedel and Crafts reaction of aryl ethers and succinic anhydride was run on 27 ethers. Satisfactory derivatives were obtained with 20 of these ethers.

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