[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY,
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THE FRIEDEL AND CRAFTS REACTION IN QUALITATIVE ORGANIC CHEMISTRY. II. AROYL PROPIONIC ACIDS OF AROMATIC HYDROCARBONS

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As a part of a general study of the applicability of the Friedel and Crafts reaction in qualitative organic chemistry, the succinoylation of aryl hydrocarbons has been investigated. An excellent summary of "The Friedel and Crafts Reaction with Aliphatic Dibasic Anhydrides" by Berliner (1) indicated that the succinoylation of aryl hydrocarbons gave good yields. Reduction of this reaction to a small scale would provide a derivative in addition to the aroylbenzoic acids.

A procedure which was suggested by Berliner (1) was used. The reaction was run with mechanical stirring at room temperature with tetrachloroethane as a solvent, or at ice-bath temperatures with nitrobenzene. The attempt by one of us, Sylvia Taylor, to use carbon disulfide as a solvent in order to avoid solvent removal by steam-distillation was unsuccessful. The use of carbon disulfide gave products which frequently were oils and the yields were generally smaller. The solvent of choice was tetrachloroethane for alkylbenzenes, diphenyl and fluorene, while fair results were obtained with naphthalene, tetralin, and α- and β-methylnaphthalene. Nitrobenzene gave good results with acenaphthene, tetralin, α- and β-methylnaphthalene, naphthalene, and diphenylmethane.

The reaction procedure gave poor results or failed with the following compounds: *p*-xylene, *p*-dicyclohexylbenzene, *p*-di-*tert*-butylbenzene, *p*-cymene, dibenzyl, *o*-, *m*-, *p*-terphenyl, triphenylmethane, phenanthrene, and anthracene. Several of these compounds gave derivatives, but the yields were too low and the compounds were not sufficiently pure to be useful for identification work.

The neutral equivalent of each derivative was determined to show that the expected compound was obtained. Oxidation of the carbonyl-containing side chain by NaOCl or NaOBr was carried out to determine the position of substitution. Alkaline permanganate was used on the *sec*-amylbenzene derivative when the hypochlorites gave low-melting solids. The terephthalic acid obtained was identified by its *p*-bromophenacyl ester. The *para* position was the point of substitution for monoalkylbenzenes. The substitution of the 1,2,4-triethylbenzene was assumed to be on the 5th carbon. Although a sharp melting point was obtained for a triethylbenzoic acid, no literature value with which to compare it was found. Attempted oxidation to a known benzene tetracarboxylic acid by means of alkaline permanganate gave negative results.

The β-aroylpropionic acids of aromatic hydrocarbons are recommended as derivatives: (a), The yield of the derivative is fairly high, (b), the derivative is pure, (c), the melting point spread is large enough to readily identify the hydro-

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[1] Taken from a portion of the thesis submitted by Sylvia Taylor to the College of Wooster in partial fulfillment of the requirements for the B.A. degree.

TABLE I

Aroyl Propionic Acids of Aromatic Hydrocarbons

HYDROCARBON USED	B.P., °C.	DERIVATIVE, M.P., °C.		DERIVATIVE NEUTRAL EQUIV.[e]		CRUDE YIELD, %	RECRYSTALLIZATION METHOD	REACTION PROCEDURE
		Obsv'd	Lit. Ref.	Obsv'd	Calc'd			
Benzene	80	116.5–117.5	116 (3)	178.3	178.2	60	B	I
Toluene	111	127–128.5	129 (4)	193.5	192.2	79	B	I
Ethylbenzene	135	107–108.5	107–108 (5)	207.2	206.2	44	A, B	I
m-Xylene	139	112–113	114 (4)	207.0	206.2	65	B	I
o-Xylene	142	130–131	129 (4)	206.8	206.2	72	B	I
Cumene	153	139.5–141.5	141–142 (4)	220.0	220.3	82	B	I
n-Propylbenzene	158	120.5–122.5	120–121 (6)	221.4	220.3	82	B	I
Mesitylene	164	109–109.5	109 (7)	221.2	220.3	54	C, B	I
tert-Butylbenzene	169	123.5–125	126 (8)	234.7	234.3	56	B, A	I
sec-Butylbenzene	173	95.5–96.5		234.7	234.3	67	A, B	I
n-Butylbenzene	183	111–112.5	115–116 (9)	234.9	234.3	85	B	I
sec-Amylbenzene	187	74–76		247.7	248.3	83	A	I
Tetralin	206	121–122	120–121 (10)	232.3	232.3	69	A, B	II, I
1,2,4-Triethylbenzene	218	124.0–125.5		261.7	262.4	70	C, B	I
Phenylcyclohexane	237	136–136.5	134 (11)	263.0	259.4	74	C, B	I
α-Methylnaphthalene	240	168.5–169.5	168–169 (12)	244.4	241.2	42	B	II
Diphenylmethane	265	125–126	125–126 (13)	271.2	268.8	31	B	II
β-Methylnaphthalene	32[b]	165–166	168 (14)	242.4	241.2	53	B	II
Diphenyl	70[b]	183.5–185	185 (15)	251.4	254.4	74	C, B	I
Naphthalene	80[b]	172–173	172 (16)	230.5	227.2	74	B	II, I
Acenaphthene	95[b]	209–210	208 (17)	252.7	254.4	54	C	II
Fluorene	115[b]	212–213	210–212 (18)	264.4	266.3	73	C	I

[a] All melting points were taken with a calibrated thermometer. [b] Melting point. [c] A, Recrystallized from ligroin or benzene-ligroin. B, Recrystallized from alcohol. C, Sodium salt recrystallized from water. [d] The melting and boiling points of the hydrocarbons were taken from Shriner and Fuson (2). [e] The neutral equivalents of the acids were taken by dissolving the acid in hot alcohol and titrating immediately with aqueous NaOH. The indicator was phenolphthalein.

carbons, (d) the neutral equivalents may be determined for a further property of the derivative, and (e) the possibility of a sodium hypochlorite oxidation to a known benzoic acid exists.

PROCEDURE

I. Tetrachloroethane as a solvent. The molar ratio of hydrocarbon: anhydride: aluminum chloride was 1:1:2. Tetrachloroethane (20 ml.) was added to the succinic anhydride in a 25 × 150 mm. test tube. The mixture was heated to dissolve the succinic anhydride, then cooled to room temperature. One gram of the hydrocarbon was added, and mechanical stirring, which consisted of a 300 r.p.m. synchronous motor attached to a propeller type stirrer was used. (If the hydrocarbon was a solid, it was placed in the test tube with the succinic anhydride before heating.) Anhydrous aluminum chloride was added over a period of 20 minutes, and the mechanical stirring was continued for 2–3 hours. The reaction could be allowed to stand or be decomposed immediately. The reaction mixture was decomposed by slowly pouring it into a 200-ml. round-bottomed flask which contained one ice cube and 10 ml. of 6 *N* HCl. Water was then added to the flask until the volume was about 125 ml., and the contents were boiled until all the tetrachloroethane was removed. The flask was cooled, the contents were filtered, and the precipitate was thoroughly washed with cold water. The precipitate was returned to the 200-ml. flask, and 10 ml. of 10% Na_2CO_3 and 50–75 ml. of water were added. The contents of the flask were then heated to boiling (caution, foaming!), decolorized with charcoal, and filtered hot. The filtrate was cooled, (the sodium salt may precipitate at this point), acidified with 6 *N* HCl, and the precipitate was filtered and washed with cold water. The derivative could be recrystallized from alcohol or ligroin.

II. The procedure using nitrobenzene as a solvent was the same as that above with the following modifications: The reaction was run at ice-bath temperatures; the hydrocarbon was added last and dropwise to the reaction mixture; and the reaction was allowed to stand for 2 days or more at room temperature before decomposition. It was necessary that all of the nitrobenzene be removed in order that the derivative would solidify when the steam distillation was complete.

The purification of these derivatives was best accomplished by recrystallization of the sodium salt from water or a dilute NaCl solution if this salt were slightly soluble. Ligroin, or a benzene-ligroin mixture was the best solvent for derivatives which melted below 100°, while alcohol or dilute alcohol gave excellent results for the higher-melting derivatives.

β-(p-tert-Butylbenzoyl)propionic acid. One hundred ml. of a solution which contained 40 ml. of 5.25% NaOCl and 2.0 g. of NaOH was added to 0.95 g. of the keto acid. The flask was warmed in a water-bath for 15 minutes, then refluxed for 15–20 minutes more. The flask was cooled, and solid Na_2SO_3 was then added. After acidification with 6 *N* HCl, the precipitate was washed with cold water and was recrystallized from dilute alcohol. The melting point of the substituted benzoic acid obtained was 166–167.5°, while the recorded melting point of *p-tert*-butylbenzoic acid is 165–165.6° (19).

β-(p-n-Butylbenzoyl)propionic acid. Oxidation. The method of oxidation used was that of Zaki and Fahim (20). The substituted benzoic acid obtained melted at 102.5–103°, while the melting point of *p-n*-butylbenzoic acid is 101° (20).

β-(p-sec-Butylbenzoyl)propionic acid. Oxidation. The oxidation was carried out as with the *n*-butylbenzene derivative. The substituted benzoic acid obtained melted at 92.5–94° (21). Since the melting point of the oxidation product was so close to that of the starting material, a mixture melting point was taken. This gave a range of 56–84°. The neutral equivalent of the product was 180.9, while the neutral equivalent is 178.2 for *p-sec*-butylbenzoic acid.

β-(1,2,4-Triethylbenzoyl)propionic acid. Oxidation. The oxidation of this acid was accomplished by the same procedure as was used with the *tert*-butylbenzene derivative. The substituted benzoic acid obtained melted at 75–77° and its neutral equivalent was 208.1 (Calc'd 206.2). Since no literature melting point was available, an alkaline permanganate oxidation was tried on the original compound. No solid was obtained.

β-(p-sec-Amylbenzoyl)propionic acid. Oxidation. Attempted oxidation by NaOCl and NaOBr gave oils which slowly solidified. Alkaline permanganate was then applied, and the *p*-bromophenacyl ester of the acid product was prepared. The ester had m.p. 222–225.5°, while the literature value for the *p*-bromophenacyl ester of terephthalic acid is 225° (22). The esters of phthalic and isophthalic acids melt at 153° and 186° respectively.

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SUMMARY

The Friedel and Crafts reaction of aryl hydrocarbons and succinic anhydride was run on 31 hydrocarbons. Satisfactory derivatives were obtained with 22 of these hydrocarbons.

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