The Friedel and Crafts Reaction in Qualitative Organic Chemistry. III. Aroyl Benzoic Acids of Aromatic Ethers

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As a part of a general study of the applicability of the Friedel and Crafts reaction to qualitative organic chemistry, the benzoylation of aromatic ethers has been investigated.

An adaptation of the procedures of Underwood and Walsh[3] with carbon bisulfide as a solvent failed. The yields were low as was the purity of the products. Procedures in which *sym*-tetrachloroethane was used as a solvent at room temperature and at 50° gave better results. The products of the room temperature procedure were purer, though the yields were slightly lower. The procedure which gave the best results used a solvent mixture of 80% *sym*-tetrachloroethane and 20% nitrobenzene recommended by Berliner[4] for succinoylation. This procedure was successful for 19 ethers. It failed for *m*-cresyl methyl ether and *o*-methoxybiphenyl due to low purity of product; for *p*-chloroanisole, *p*-bromoanisole and *p*-chlorophenetole due to very low yield; for *p*-ethoxybiphenyl and *p*-methoxybiphenyl due to the low solubility of the sodium salt.

Table I

Aroyl Benzoic Acids of Aromatic Ethers

Ether used[a]	Crude yield, %	Derivative m.p., °C.[b]		Deriv. formula	Carbon, %		Hydrogen, %		Neut. equiv.	
		Obsd.	Lit.		Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
Anisole	65	147–148	148[c]	$C_{15}H_{12}O_4$					255.9	256.2
Phenetole	64	134.8–135.5	135–136[d]	$C_{16}H_{14}O_4$					268.2	270.2
p-Cresyl methyl	25	157.5–158.5	122[e]	$C_{16}H_{14}O_4$	70.73	71.11	5.29	5.22	269.7	270.2
o-Cresyl ethyl	80	157–157.7		$C_{17}H_{16}O_4$	71.63	71.80	5.43	5.68	284.5	284.3
m-Cresyl ethyl	80	121.4–121.7		$C_{17}H_{16}O_4$	71.64	71.80	5.75	5.68	283.4	284.3
p-Cresyl ethyl	31	153.5–154.5		$C_{17}H_{16}O_4$	71.58	71.80	5.71	5.68	282.7	284.3
Veratrole	22	239–241	236–237[f]	$C_{16}H_{14}O_5$					283.4	286.3
o-Chlorophenetole	37	186–186.8		$C_{16}H_{13}O_4Cl$	62.90	63.06	4.29	4.30	306.3	304.8
n-Butyl phenyl	66	119–120		$C_{18}H_{18}O_4$	72.34	72.47	6.19	6.10	297.0	298.3
Resorcinol dimethyl	60	162.5–164.5	164–165[g]	$C_{16}H_{14}O_5$					284.8	286.3
o-Bromoanisole	32	188.5–189.5[k]		$C_{15}H_{11}O_4Br$	53.81	53.91	3.45	3.32	334.2	333.2
o-Bromophenetole	29	179–181		$C_{16}H_{13}O_4Br$	55.33	55.03	3.93	3.75	350.5	349.2
Resorcinol diethyl	63	174.5–176	175–176[h]	$C_{18}H_{18}O_5$					314.6	314.3
Phenyl	65	161–162.5	163.5[i]	$C_{20}H_{14}O_4$					317.7	318.3
Ethyl α-naphthyl	80	158–159		$C_{20}H_{16}O_4$	75.31	74.98	5.29	5.04	321.0	320.3
Ethyl β-naphthyl	82	203–203.5		$C_{20}H_{16}O_4$	74.71	74.98	4.95	5.04	319.9	320.3
Resorcinol dibutyl	71	164–164.5		$C_{22}H_{26}O_5$	71.13	71.33	7.00	7.08	370.9	370.4
p-Bromophenyl phenyl	48	197.5–199		$C_{20}H_{13}O_4Br$	60.44	60.47	3.05	3.30	397.7	397.2
Methyl β-naphthyl	78	197.5–198.5	198[j]	$C_{19}H_{14}O_4$					304.7	306.3

[a] The ethers are arranged in order of boiling and melting points. [b] All melting points were taken with a calibrated thermometer. [c] H. Meyer and R. Turnau, *Monatsh.*, **30**, 481 (1909). [d] E. Grande, *Gazz. chim. ital.*, **20**, 124 (1890). [e] W. H. Bentley, H. D. Gardner and C. Weizmann, *J. Chem. Soc.*, **91**, 1633 (1907). [f] M. A. Haq and J. N. Ray and M. Tuffail-Malkana, *ibid.*, 1327 (1924). [g] W. R. Orndorf and E. Kline, This Journal, **46**, 2287 (1924). [h] C. Graebe, *Ber.*, **28**, 28 (1895). [i] H. Kipper, *ibid.*, **38**, 2392 (1905). [j] Ch. Weizmann and E. Bergmann, *J. Chem. Soc.*, 567 (1936). [k] When recrystallized from acetic acid, m.p. is 195–196°.

In general, the aroyl benzoic acids make fair derivatives of ethers. Their melting points are high, the melting point spread for successive ethers in a series is large enough for identification, the yields are fair and they may be purified readily. Their principal disadvantage is the tendency of the acid to crystallize slowly when it is precipitated from sodium carbonate solution.

A comparison with the succinoylation reaction of aryl ethers[5] shows that the latter reaction is superior in most cases. The reaction proceeds smoothly for both anhydrides if the *para* position is open, but the yields are better with succinoylation. If the *para* position is blocked, derivatives are obtained in poor yields, 20–25%, with succinoylation while the benzoylation gives no reaction under these conditions. The β-aroyl propionic acids crystallize much more quickly when first precipitated. The β-naphthyl ethers give satisfactory derivatives with benzoylation under these conditions where succinoylation leads to a mixture of isomeric products.

Experimental

Procedure.—The procedure followed was that of Reinheimer and Smith[5] with phthalic anhydride replacing succinic. The oily precipitate which resulted from the acidification of the sodium carbonate solution was allowed to stand overnight in a refrigerator, rather than a few minutes, before filtration. The solid acid may be recrystallized from ethanol or dilute ethanol, glacial acetic acid or dilute glacial acetic acid. The derivatives are more soluble in ethanol so that the higher melting derivatives are best recrystallized from it.

The acids were dried in a vacuum desiccator over Drierite.

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(2) From the Independent Study Theses of Clarence R. Bresson, 1950, Alice J. Holloway, 1954, and C. Raymond Dailey, 1954.

(3) H. W. Underwood, Jr., and W. L. Walsh, This Journal, **57**, 940 (1935).

(4) R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1949, Vol. 5, p. 257.

(5) J. D. Reinheimer and J. C. Smith, *J. Org. Chem.*, **17**, 1505 (1952).