The 6-acetaminoindole was also obtained in good yield by treating an aqueous solution of 6-aminoindole hydrochloride with acetic anhydride and sodium acetate.[8]

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Acylation of Alkyl Aryl Ethers with Iodine as Catalyst

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Acylation with iodine as a catalyst,[1,2] gives good yields of some alkoxy-substituted aceto-, propio-, isobutyro-, butyro- and caprophenones, although the acetylation of phenyl acetate, guaiacol, guaiacol acetate and bromo- and iodobenzene is unsuccessful. We have confirmed the report that anisole does not react with succinic anhydride in the presence of iodine.[3] The preparation of 4-methoxyacetophenone, reported by Chodroff and Klein,[3] who used a mole excess of anisole, has been improved.

Our experiments and those of Kaye, *et al.*,[4] indicate that iodine can be used as a catalyst for the acylation of aromatic ethers by aliphatic or aromatic monocarboxyl chlorides or anhydrides, and that this method is better for the preparation of alkoxy aryl ketones than the conventional Friedel–Crafts procedure. In successful acylations, the violet colored vapor of the refluxing mixture disappeared after 15–30 minutes, but when there was no reaction, the color persisted.

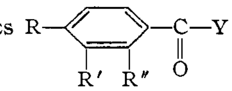
Experimental[5]

General Procedure, 4-Methoxyacetophenone.—A mixture of 21.6 g. (0.2 mole) of anisole, 22.5 g. (0.22 mole) of acetic anhydride and 1.0 g. (0.004 mole) of iodine was refluxed for three hours. The dark brown solution was poured into 100 ml. of water. The mixture was extracted with ether; the ether solution was washed successively with dilute sodium carbonate, sodium bisulfite and water and then dried over sodium sulfate. After removal of the solvent and distillation of the residue under vacuum, 24 g. (80%) of 4-methoxyacetophenone was obtained, b.p. 120–125° (5 mm.). The yield was 50% when acetyl chloride was used. After crystallization from aqueous methanol the compound melted at 37–38° and its semicarbazone at 197–198°; reported m.p. 38°, semicarbazone m.p. 198–198.5°.[3]

In the presence of 0.8 g. (0.00278 mole), 1.2 g. (0.0047 mole), 1.6 g. (0.0063 mole), 0.2 g. (0.00079 mole) of iodine, a mixture of 0.2 mole of anisole and 0.22 mole of acetic anhydride, gave yields of 68.7, 66, 61.2 and 45%, respectively.

2-Methoxy-1-acetylnaphthalene.—A mixture of 15.8 g. (0.1 mole) of 2-methoxynaphthalene, 11.3 g. (0.11 mole) of acetic anhydride and 0.5 g. (0.00196 mole) of iodine gave after recrystallization from dilute alcohol, 13.2 g. (63%) of 2-methoxy-1-acetylnaphthalene, m.p. 57°; its mixed m.p. with an authentic specimen was 57–58°; reported by Noller and Adams,[6] 57–58°.

TABLE I

KETONES 

R[a]	R′	R″	Y	Yield, %	M.p., °C.	Semicarbazone m.p., °C.
CH_3O	CH_3O	H	Methyl	66.5	47–48[b]	209–211[c]
CH_3O	H	CH_3O	Methyl	71	42–43.5[d]	211–213[e]
C_2H_5O	H	H	Methyl	66	36–37.5[f]	179–180[g]
CH_3O	H	H	Ethyl	50	26–27[h]	171–172[i]
CH_3O	CH_3O	H	Ethyl	46.5	56–58[j]	191[k]
C_2H_5O	H	H	Ethyl	57	29–30[l]	181–183[m]
CH_3O	H	H	Propyl	68	19–21[n]	179–181[o]
CH_3O	CH_3O	H	Propyl	74	59–61[p]	178–180[q]
CH_3O	H	H	*i*-Propyl	42	[r]	202–203[s]
CH_3O	H	H	Pentyl	49.3	38–39[t]	143[u]

[a] All compounds were recrystallized from aqueous methanol. [b] C. Mannich, *Arch. Pharm.*, **248**, 137 (1910), reports m.p. 48°. [c] Ref. *b*, m.p. 211°. [d] J. Tambor, *Ber.*, **43**, 1884 (1910), reports 44°. [e] *Anal.* Calcd. for $C_{11}H_{15}O_3N_3$ (237.25): N, 17.71. Found: N, 17.64. [f] F. Unger, *Ann.*, **504**, 267 (1933), reports m.p. 37–38°. [g] Ref. *f*, m.p. 181.5°. [h] Ref. *f*, m.p. 29°. [i] Ref. *f*, m.p. 172°; F. v. Wessely, *et al.*, *Monatsh.*, **73**, 127 (1940), give m.p. 175°. [j] R. D. Haworth and D. Woodcock, *J. Chem. Soc.*, 809 (1938), reports m.p. 58–59°. [k] E. Martegiani, *Gazz. chim. ital.*, **42**, II, 348 (1912), reports m.p. 190–192°. [l] L. Gattermann, R. Ehrhardt and H. Maisch, *Ber.*, **23**, 1205 (1890), reports m.p. 30°. [m] *Anal.* Calcd. for $C_{12}H_{17}O_2N_3$ (235.28): N, 17.46. Found: N, 17.31. The *p*-nitrophenylhydrazone melted at 163–164°. *Anal.* Calcd. for $C_{17}H_{19}O_3N_3$ (314.32): N, 13.37. Found: N, 13.30. [n] P. M. Baranger, *Bull. soc. chim.*, [4] **49**, 1213 (1931), reports m.p. 21–22°. [o] Ref. *n*, m.p. 183°; ref. *f*, m.p. 173.5°. [p] *Anal.* Calcd. for $C_{12}H_{16}O_3$ (208.29): C, 69.21; H, 7.74. Found: C, 69.30; H, 7.55. [q] *Anal.* Calcd. for $C_{13}H_{19}O_3N_3$ (265.29): N, 15.84. Found: N, 15.63. [r] B.p. 188–190° (40 mm.): A. Sosa, *Ann. chim.*, **14**, 5 (1940), reports b.p. 158.5–159.5° (12 mm.). [s] Ref. *r*, m.p. 193–194° (heating block) and 206°. [t] S. Skraup and F. Nieten, *Ber.*, **57**, 1295 (1924), report m.p. 41°. [u] Ref. *f*, m.p. 142.5°.

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Furfuryl Esters of Some Dicarboxylic Acids

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Earlier authors[2–7] have prepared furfuryl esters of monocarboxylic acids by a variety of methods, none of which appears to be suitable for the difurfuryl esters of dicarboxylic acids. The reactions of furfuryl alcohol with phthalic and succinic anhydrides give the mono esters. In the present work we found that the difurfuryl esters lacked sufficient volatility and thermal stability to make

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