Relative Reactivities of Acyl Chlorides in the Friedel–Crafts Acylation of Benzene and Mesitylene

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COMPARATIVE data on the reactivities of acyl chlorides in the Friedel–Crafts acylation reaction have mainly been of a qualitative kind.[1] A sequence of reactivities, acetyl chloride > benzoyl chloride > 2-ethylbutyryl chloride, has been found for aluminium chloride-catalysed acylations of toluene.[2] The order benzoyl chloride > butyryl chloride > propionyl chloride > acetyl chloride is said to apply to titanium tetrachloride-catalysed acylations of benzene, toluene, or anisole.[3] More recently kinetic data for the acylation of toluene have been determined for a series of substituted benzoyl chlorides.[4]

We now report a study of the relative acylation rates of six acyl chlorides in the presence of aluminium chloride with benzene and mesitylene. In chloroform, ethylene chloride, or carbon disulphide as solvent, the formation of diacylmesitylenes becomes important, whereas in nitromethane diacylation is suppressed.[5] Table 1 shows a set of rates of propionylation relative to acetylation with mesitylene, and the proportions of diacyl derivatives formed, in nitromethane over a 60° temperature range. The data given in Table 2 show that acylation rates in nitromethane solvent decrease in the sequence acetyl > propionyl > butyryl > isobutyryl > benzoyl > 2,4,6-trimethylbenzoyl chlorides, with substrates mesitylene and benzene. In this solvent, as in nitrobenzene, the equilibrium

$$RCOCl,AlCl_3 + MeNO_2 \rightleftharpoons RCOCl + MeNO_2,AlCl_3$$

is likely to favour the free acyl chloride rather than an oxonium complex.[6] A relative rate of acetylation of mesitylene and benzene (= 2250) has previously been obtained, with nitromethane as solvent at 25°.[7] This means that the acylation rates reported here span a ratio of about 10^6. Alkyl substitution lowers the reactivity of an aliphatic or aromatic acyl chloride, and this effect is more pronounced in the mesitylene series. Both benzene and mesitylene were found to react with 2,4,6-trimethylbenzoyl chloride at low but significant rates, whereas earlier attempts thus to acylate these hydrocarbons had failed.[8] It had been concluded that in a successful acylation of anisole[8] the reacting species is not the oxonium complex ($RCOCl,AlCl_3$), which would be sterically hindered and completely inert, but the trimethylbenzoyl cation,[8–10] having a comparatively low reactivity. In the present system the mechanism of acylation may range from an attack by an oxonium complex (possibly solvated)[10,11] (as in acetyl chloride–benzene) to an attack by an essentially free cation (as in trimethylbenzoyl chloride–mesitylene). More detailed investigations are in progress.

TABLE 1

Relative rates of acylation of mesitylene in nitromethane

Temperature	Rate (EtCOCl)/ Rate (MeCOCl)	Diacylmesitylenes (yield, %)
−20°	0·35	<0·001
0°	0·30	0·075
20°	0·22	4·3
40°	0·21	4·9

TABLE 2

Relative reactivities of acyl chlorides in the aluminium chloride-catalysed acylations of benzene and mesitylene in nitromethane at 0°.

Acyl Chloride	Rate (RCOCl)/Rate (MeCOCl)	
	Benzene	*Mesitylene*
R = Me	1·00	1·00
Et	0·92	0·30
Pr	0·80	0·27
Pr^i	0·20	0·18
Ph	0·06	0·35
Mesityl	0·0018	0·00013

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