Aromatic Acylations catalysed by Metal Oxides

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Dimethylbenzophenones are obtained in high yield from reactions between benzoyl chloride and each of the three isomeric xylenes during 10 h at 150 °C in the presence of small amounts of iron(III) oxide, zinc oxide, ammonium molybdate, tin(II) oxide, molybdenum(VI) oxide, or sodium tungstate. Oxides of titanium, aluminium, chromium, manganese, vanadium, thorium, copper, zirconium, tungsten, and ammonium vanadate are ineffective under these conditions. The benzoylation of 1,4-xylene also occurs in the presence of iron, iron(II) sulphate, iron(III) sulphate, and iron(III) chloride. Iron(III) oxide catalyses the benzoylation of anisole, alkylbenzenes, and halogenobenzenes to give the appropriate 4-substituted benzophenones in high yield. 1,3-Xylene undergoes acylation and sulphonylation with reagents such as chloroacetyl chloride and benzenesulphonyl chloride, respectively, in the presence of ammonium molybdate to give the appropriate acetophenone or aromatic sulphone. The relative rates of the reaction between benzoyl chloride and 1,4-xylene in the presence of most of the catalysts mentioned have been assessed by estimating the amount of hydrogen chloride evolved.

CONSIDERABLE attention has been focused on the synthesis of aromatic ketones from Friedel–Crafts reactions between acyl halides and a variety of aromatic substrates in the presence of at least 1 mol. equiv. of a Lewis acid such as aluminium chloride.[1] Reactions of this type, especially between benzoyl chloride and reactive substrates such as aryl ethers and polycyclic arenes, also proceed readily in the presence of small amounts of catalysts such as metals, metal chlorides, and iodine, to give the appropriate benzoylated products in high yield.[2]

TABLE 1

Preparation of dimethylbenzophenones from reactions between benzoyl chloride (140 g, 1 mol) and xylene (159 g, 1.5 mol) at 150 °C for 10 h catalysed by metal oxides

Substrate	Catalyst [a]	Conversion (%) [b]	Benzophenone	Yield (g; %) [c]
1,2-Xylene	ZnO	100	3,4-Me_2 (I)	185; 88.0 [d]
	Fe_2O_3	100		185; 88.0
	Na_2WO_4	52		92; 84.2
	SnO	100		172.8; 81.8
1,3-Xylene	ZnO	100	2,4-Me_2 (II)	191.3; 91.0
	Fe_2O_3	100		186.6; 88.7
	$(NH_4)_6Mo_7O_{24},4H_2O$	100		193.4; 92.0
	SnO	100		191.4; 91.0
	Na_2WO_4	41		72.7; 85.6
1,4-Xylene	Fe_2O_3	100	2,5-Me_2 (III)	176.2; 83.8
	MoO_3	98		181.7; 88.2
	SnO	66		116.3; 83.8
	ZnO	100		176.5; 83.9 [e]
	ZnO	100		198.5; 94.5
	ZnO	100		202.7; 96.5 [f]

[a] Quantities used were as follows: ZnO (2.0 g, 25 mmol); Fe_2O_3 (1.60 g, 10 mmol); Na_2WO_4 (5.88 g, 20 mmol); SnO (2.69 g, 20 mmol); $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (3.55 g, 3.0 mmol); MoO_3 (2.88 g, 20 mmol). [b] Of benzoyl chloride. [c] Based on benzoyl chloride consumed. [d] Ref. 3. [e] 1,4-Xylene (105 g, 1 mol) used. [f] 1,4-Xylene (318 g, 3 mol) used.

An investigation is reported here of the activities and synthetic utility of a number of metal oxides in Friedel–Crafts reactions of the type described above. Metal oxides are particularly useful as catalysts in this respect since they are readily available, inexpensive, generally non-corrosive, and non-hygroscopic. It has been shown that zinc oxide catalyses the benzoylation of 1,2-xylene to give 3,4-dimethylbenzophenone in high yield,[3] but the activities of other metal oxides in aromatic acylation have not been explored.

The aromatic acylations were carried out at 150 °C for 10 h with an excess of the substrate and up to 20 mmol. equiv. of the appropriate metal oxide. The products were isolated by vacuum distillation, purified by either redistillation or recrystallisation, and identified by a combination of mass spectrometry, ^1H n.m.r. spectroscopy, and elemental analysis. Initially, an examination of the benzoylation of each of the three isomeric xylenes (1.5 mol) with benzoyl chloride (1.0 mol) showed that the appropriate dimethylbenzophenone is produced in high yield in the presence of zinc oxide, iron(III) oxide, sodium tungstate, tin(II) oxide, ammonium molybdate, or molybdenum(VI) oxide (Table 1). No reaction is observed with any of the xylenes under the same conditions in the absence of a catalyst (limit of detection 2%). The highest yields were obtained with 1,3-xylene, though none of the reactions has been optimised. However, from the synthetic aspect, an excess of hydrocarbon substrate is desirable for efficient benzoylation: the highest yields of dimethylbenzophenone are obtained when at least a 50% excess of xylene is employed. The results obtained with 1,4-xylene and zinc oxide as catalyst are shown in Table 1. Sodium tungstate is the least effective catalyst of those

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[1] See, for example, P. H. Gore, ' Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. 3, part 1, pp. 1—382, and references cited therein.

[2] D. E. Pearson and C. A. Buehler, *Synthesis*, 1972, 533.

[3] U.S.P. 2,802,032/1957.

shown, but it is nevertheless considerably more active than the following oxides, which did not catalyse the benzoylation of 1,4-xylene during 10 h at 150 °C: titanium(IV) oxide, vanadium(V) oxide, chromium(III) oxide, manganese(IV) oxide, aluminium(III) oxide, thorium(IV) oxide, copper(II) oxide, zirconium(IV) oxide, tungsten(VI) oxide, and ammonium vanadate. Overall, the yields obtained with active metal oxides are generally higher than those obtained by the traditional Friedel–Crafts synthesis from the appropriate xylene, benzoyl chloride, and an equimolar amount of a Lewis acid. For example, 1,4-xylene and antimony trichloride give 2,5-dimethylbenzophenone in only 69% yield at 180 °C during 6 h.[4]

The benzoylation of other aromatic substrates in the presence of catalytic amounts of metal oxides was examined with iron(III) oxide as an example. Reactions were carried out at 150 °C for 10 h with 2 mol. equiv. of the substrate and 10 mmol. equiv. of the catalyst. The results obtained are shown in Table 2. Anisole, ethylbenzene, and t-butylbenzene react readily during 10 h at 150 °C to give the appropriate 4-substituted benzophenone [compounds (IV)—(VI)] in high yield. However, benzoylation is inhibited when powerful electronegative substituents are present in the substrate; neither benzoic acid nor nitrobenzene reacts to give substituted products, although a significant quantity of benzoic anhydride (VII) is formed in the first case. In contrast, less deactivated aromatic compounds such as bromo-, chloro-, and iodo-benzene all react with benzoyl chloride to give the appropriate 4-halogenobenzophenone, (VIII)—(X). The partial conversion of benzoyl chloride observed under these conditions probably reflects the deactivating influence of the halogeno-substituent. Indeed, the presence of two halogeno-substituents, *e.g.* in 1,4-dibromobenzene, results in little or no benzoylation.

TABLE 2

Preparation of substituted benzophenones from reactions between benzoyl chloride (70 g, 0.5 mol) and substituted benzenes (1.0 mol) catalysed by iron(III) oxide (5 mmol) at 150 °C for 10 h

Substrate	Conversion (%) [a]	Product *	Yield (g; %) [b]	B.p. (°C at 3—4 mmHg)
PhOMe	100	4-MeO-BP (IV) [c]	89.8; 84.7	193—195
EtPh	100	4-Et-BP (V)	87.2; 83.1	173—173
Bu^tPh	100	4-Bu^t-BP (VI)	99.6; 83.7	185—186
$PhCO_2H$	46.7	$(Bz)_2O$ (VII) [d]	43.4; 82.1	191—194
PhCl	41.0	4-Cl-BP (VIII)	35.5; 80.0	162—164
PhBr	38.1	4-Br-BP (IX)	39.7; 79.7	174—176
PhI	39.7	4-I-BP (X)	46.5; 76.0	182—184
1,4-$Br_2C_6H_4$	5.2	[e]		
$PhNO_2$	8.1	[e]		

* BP = benzophenone.

[a] Of benzoyl chloride. [b] Based on benzoyl chloride consumed. [c] Same product (90.1 g, 85.0%) obtained also with ammonium molybdate (1.5 mmol) under the same conditions. [d] Identified by i.r. spectroscopy. [e] None isolated.

The activity of ammonium molybdate in aromatic acylation and sulphonylation reactions was also examined, with 1,3-xylene as substrate. Reactions were again carried out at 150 °C for 10 h with 2 mol. equiv. of substrate and 3 mmol. equiv. of catalyst. The results obtained are shown in Table 3. Chloroacetyl chloride reacts with the xylene under these conditions to give 2-chloro-2′,4′-dimethylacetophenone (XI) in moderate yield, but hexanoyl chloride reacts less rapidly, and only a partial conversion into the hexanophenone (XII) occurs. Whereas phenylacetyl chloride reacts with the xylene to give the 2-phenylacetophenone derivative (XIII), along with considerable amounts of phenylacetic acid, trimethylacetyl chloride does not react. Although benzenesulphonyl chloride and its 4-methyl derivative give the appropriate diphenyl sulphone in high yield [(XIV) and (XV)] there is no significant reaction with methanesulphonyl chloride. The presence of either electron-donating or electron-withdrawing substituents in benzoyl chloride appears to have little effect on the benzophenone yield in a reaction for 10 h, although the rates of reaction are almost certainly different. Thus, 3-nitro-, 4-chloro-, 4-methoxy-, and 4-methyl-benzoyl chlorides all give the appropriate 2,4-dimethylbenzophenone in good yield [compounds (XVI)—(XIX)].

DISCUSSION

The failure of oxides such as those of aluminium and titanium, and success of others such as zinc and iron, to catalyse the benzoylations described is puzzling, since all the respective halides are powerful Friedel–Crafts reagents.[1] However, whereas most of the oxides employed were commercial samples, iron(III) oxide was freshly prepared by calcining the hydroxide in air at 700 °C for 1 h. A number of the oxides examined, including those of aluminium and titanium, are known to be inert to a variety of reagents, such as strong acids and bases, because of the crystal form produced at the high temperatures at which they are normally prepared. Since the lack of activity observed with these oxides in benzoylations could be a reflection of their inertness, fresh samples of both aluminium and titanium oxides were prepared by calcining the respective hydroxides in air at 700 °C for 1 h. Both oxides, however, again failed to catalyse the benzoylation of 1,4-xylene.

The benzoylations catalysed by iron(III) oxide generally proceed in high yield (Table 2), except in those cases where a strongly deactivating substituent is present in the substrate. These results are not unusual: a similar picture is observed for the more traditional syntheses where equimolar quantities of Lewis acids such as aluminium chloride are employed as catalysts. For example, nitroarenes are unreactive except when an activating group is also present.[1] Aromatic carboxylic acids behave similarly, though the reaction described here produces a high yield of benzoic anhydride.

The acylations and sulphonylations catalysed by

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[4] L. F. King, *J. Appl. Chem.*, 1965, **15**, 449.

ammonium molybdate proceed readily when an aromatic nucleus or an electron-withdrawing group such as chloromethyl is attached to the carbonyl or sulphonyl function. Thus, both benzoyl chloride and benzenesulphonyl chloride and their ring-substituted derivatives give high yields of the appropriate products with 1,3-xylene (Table 3). Trimethylacetyl chloride, methanesulphonyl chloride, and hexanoyl chloride are much less reactive with this catalyst; only the last reagent gives a substituted product. The reason for the reduction in chemical reactivity is not clear since it appears to follow the opposite trend to that established for related reactions which utilise equimolar amounts of Lewis acids.[1]

TABLE 3

Preparation of substituted ketones and sulphones from reactions between 1,3-xylene (106 g, 1 mol) and acid chlorides (0.5 mol) catalysed by ammonium molybdate (1.5 mmol) at 150 °C for 10 h

Acid chloride	Product	Yield (g; %)	B.p. (°C at 3—4 mmHg)
Chloroacetyl	2-Chloro-2′,4′-dimethylacetophenone (XI)	62.5; 68.5	122—126
Hexanoyl	2,4-Dimethylhexanophenone (XII) [a]	10.1; 33.0	165—175
Phenylacetyl	2′,4′-Dimethyl-2-phenylacetophenone (XIII)	46.2; 41.3	161—163
	Phenylacetic acid [b]	17.3; 25.4	
Trimethylacetyl	None isolated [c]		
Benzenesulphonyl	Phenyl 2,4-xylyl sulphone (XIV)	106; 86.2	208—210
Toluene-4-sulphonyl	4-Tolyl 2,4-xylyl sulphone (XV)	110.5; 85.0	222—224
Methanesulphonyl	None isolated [c]		
Benzoyl	2,4-Dimethylbenzophenone	96.5; 92.0	164—166
4-Chlorobenzoyl	4-Chloro-2′,4′-dimethylbenzophenone (XVI)	99.4; 81.3	173—177
3-Nitrobenzoyl	2,4-Dimethyl-3′-nitrobenzophenone (XVII)	105.5; 82.6	199—201
4-Toluoyl	2,4,4′-Trimethylbenzophenone (XVIII)	91.8; 81.8	165—170
4-Methoxybenzoyl	2,4-Dimethyl-4′-methoxybenzophenone (XIX)	96.0; 80.0	194—196

[a] Based on hexanoyl chloride consumed (30%). [b] Identified by n.m.r. spectroscopy. [c] Little reaction: >90% of the reagent unchanged.

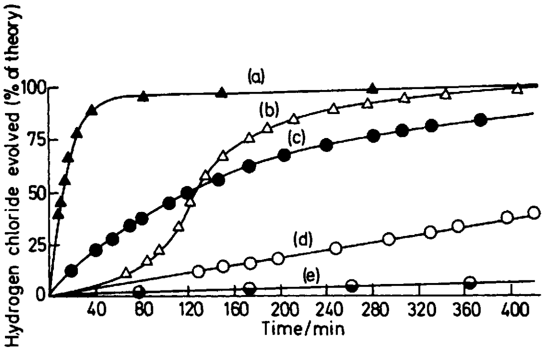

FIGURE 1

Effect of metal oxides on the rate of hydrogen chloride evolution from reactions between 1,4-xylene (1 mol) and benzoyl chloride (0.5 mol) at 150 °C: ▲ Fe_2CO_3 (5 mmol); △ ZnO (10 mmol); ● $(NH_4)_6Mo_7O_{24},4H_2O$ (1.45 mmol); ○ SnO (10 mmol); ◒ Na_2WO_4 (10 mmol)

An examination of the relative activating power of the reactive metal oxides used for benzoylation of 1,4-xylene, by estimating the amount of hydrogen chloride evolved during the reaction, shows that iron(III) oxide is the most effective catalyst studied (Figure 1). The evolution of hydrogen chloride in this case is almost linear with time and 90% of the reaction is complete within 1 h. Ammonium molybdate, tin(II) oxide, and sodium tungstate all catalyse the reaction to a much lesser degree, but zinc oxide shows a considerable induction period before the maximum rate of hydrogen chloride evolution occurs. The efficiency of other iron compounds as catalysts in the benzoylation of 1,4-xylene has also been studied (Figure 2). The activity of iron(III) sulphate is slightly greater than that of iron(III) oxide, but both are considerably more active than iron(II) sulphate, iron(III) chloride, metallic iron, and potassium hexacyanoferrate(III), which is inactive under these conditions. The lower activity of iron(III) chloride, relative to the oxide and sulphate, may be due to the formation of a weak complex with 1,4-xylene, since the chloride is soluble in the hydrocarbon at 150 °C whereas the other iron compounds are not. Indeed, when the iron atom is fully complexed as in potassium hexacyanoferrate(III), no reaction occurs. Neither iron(III) oxide nor iron(III) sulphate is apparently converted into the chloride during benzoylation: the rate of hydrogen chloride evolution observed in the two first cases is considerably greater at all times than that observed with the metal chloride.

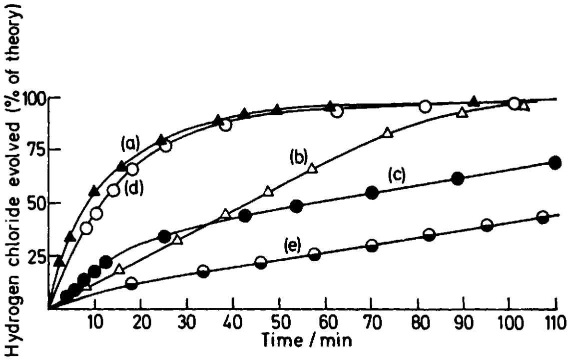

FIGURE 2

Effect of iron and its compounds on the rate of hydrogen chloride evolution from reactions between 1,4-xylene (1.0 mol) and benzoyl chloride (0.5 mol) at 150 °C: ▲ $Fe_2(SO_4)_3$ (5 mmol); △ $FeSO_4,H_2O$ (10 mmol); ● $FeCl_3$ (10 mmol); ○ Fe_2O_3 (5 mmol); ◒ Fe (10 mg atom)

TABLE 4

Elemental analysis, molecular weights, and ^{1}H n.m.r. spectra of substituted benzophenones, acetophenones, and diphenyl sulphones

		Found (%)				Calc. (%)				Chemical shifts (δ) [a]										J/Hz									
Compound	Formula	% C	% H	% Other	*M*	% C	% H	% Other	*M*	H-2	H-3	H-4	H-5	H-6	H-2′	H-3′	H-4′	H-5′	H-6′	2,3	5,6	2′,3′	2′,4′	4′,6′	5′,6′	4′,5′	2′,6′	M.p. or *b.p.* (°C)	Lit. m.p. or *b.p.* (°C)
(I)	$C_{15}H_{14}O$	85.7	6.7		210	85.7	6.7		210	7.55	2.30 (Me)	2.30 (Me)	7.15 (d)	7.55	7.75 (dd)	7.50	7.50	7.50	7.75 (dd)		8.0	8.0	2.0	2.0	8.0			47	47—48 [5]
(II)	$C_{15}H_{14}O$	85.4	6.7		210	85.7	6.7		210	2.30 (Me)	7.05	2.30 (Me)	7.05	7.45	7.75 (dd)	7.45	7.45	7.45	7.75 (dd)			8.0	2.0	2.0	8.0			*316*	*320* [5]
(III)	$C_{15}H_{14}O$	85.3	6.7		210	85.7	6.7		210	2.30 (Me)	7.15	7.15	2.25 (Me)	7.15	7.78 (dd)	7.45	7.45	7.45	7.78 (dd)			8.0	2.0	2.0	8.0			34	36 [5]
(IV)	$C_{14}H_{12}O_2$	79.3	5.9		212	79.2	5.7		212	7.80 (d)	6.90 (d)	3.80 (OMe)	6.90 (d)	7.80 (d)	7.75 (dd)	7.48	7.48	7.48	7.75 (dd)	9.0	9.0	8.0	2.0	2.0	8.0			61	61—62 [6]
(V)	$C_{15}H_{14}O$	86.0	6.7		210	85.7	6.7		210	7.74 (d)	7.26 (d)	*b*	7.26 (d)	7.74 (d)	7.78 (dd)	7.50	7.50	7.50	7.78 (dd)	8.5	8.5	8.0	2.0	2.0	8.0			*324*	*330—332* [7]
(VI)	$C_{17}H_{18}O$	86.1	7.6		238	85.7	7.6		238	7.75 (d)	7.44 (d)	1.35 (Bu^t)	7.44 (d)	7.75 (d)	7.78 (dd)	7.50	7.50	7.50	7.78 (dd)	8.0	8.0	8.0	2.0	2.0	8.0				
(VII)	$C_{13}H_9ClO$			Cl, 16.0				Cl, 16.4		7.75 (d)	7.44 (d)		7.44 (d)	7.75 (d)	7.78 (dd)	7.50	7.50	7.50	7.78 (dd)	9.0	9.0	8.0			8.0			71	75—76 [8]
(VIII)	$C_{13}H_9BrO$	59.8	3.5	Br, 30.6	260	59.3	3.3	Br, 30.6	260	7.62 (s)	7.62 (s)		7.62 (s)	7.62 (s)	7.75 (dd)	7.50	7.50	7.50	7.75 (dd)			8.0	2.0	2.0	8.0			79	81—82 [8]
(IX)	$C_{13}H_9IO$			I, 40.8				I, 41.2		7.48 (d)	7.84 (d)		7.84 (d)	7.48 (d)	7.80 (dd)	7.52	7.52	7.52	7.80 (dd)	8.0	8.0	8.0	2.0	2.0	8.0			98	100—101 [9]
(X)	$C_{14}H_{10}O_3$	74.1	4.1			74.3	4.5																					42	42 [10]
(XI)	$C_{10}H_{11}ClO$			Cl, 19.2				Cl, 19.4		2.50 (Me)	7.10	2.35 (Me)	7.10	7.55 (d)			*c*				9.0							62	62—63 [11]
(XII)	$C_{14}H_{20}O$	82.0	9.7		204	82.3	9.9		204	2.20 (Me)	6.95	2.20 (Me)	6.95	7.55 (d)			*d*				9.0								
(XIII)	$C_{15}H_{16}O$	86.1	7.2		224	85.7	7.2		224	7.22	7.22	7.22	7.22	7.22	2.42 (Me)	7.02	2.30 (Me)	7.02	7.65 (d)		9.0							*344*	*350* [12]
(XIV)	$C_{14}H_{14}O_2S$	67.9	5.9	S, 13.0	246	68.3	5.7	S, 13.0	246	2.40 (Me)	7.05 (s)	2.35 (Me)	7.18 (d)	8.10 (d)	7.85 (dd)	7.50	7.50	7.50	7.85 (dd)		8.5	8.0	2.0	2.0	8.0			84	87 [13]
(XV)	$C_{15}H_{16}O_2S$			S, 12.3	260			S, 12.6	260	2.40 (Me)	7.00 (s)	2.28 (Me)	7.15 (d)	8.06 (d)	7.72 (d)	7.22 (d)	2.32 (Me)	7.22 (d)	7.72 (d)		8.0	9.0			9.0			49	51—52 [14]
(XVI)	$C_{15}H_{13}ClO$	73.9	5.1	Cl, 14.5	244	73.6	5.4	Cl, 14.8	244	2.35 (Me)	7.05 (s)	2.30 (Me)	7.05	7.20 (d)	7.70 (d)	7.35 (d)		7.35 (d)	7.70 (d)		8.0	9.0			9.0			41	44 [15]
(XVII)	$C_{15}H_{13}NO_3$	70.2	5.2	N, 5.4	255	70.6	5.1	N, 5.5	255	2.40 (Me)	7.15 (s)	2.40 (Me)	7.10	7.25 (d)	8.56 (t)		8.10 (dd)	7.65 (t)	8.40 (dd)		8.0		1.5	1.5	8.0	8.0	1.5	63	64 [16]
(XVIII)	$C_{16}H_{16}O$	85.5	7.2		224	85.7	7.2		224	2.38 (Me)	7.05 (s)	2.30 (Me)	7.00	7.20 (d)	7.70 (d)	7.20	2.35 (Me)	7.20 (d)	7.70 (d)		8.0	8.0			8.0			*336*	*340* [17]
(XIX)	$C_{16}H_{16}O_2$	79.7	6.7		240	80.0	6.7		240	2.30 (Me)	7.05 (s)	2.25 (Me)	7.00	7.20 (d)	7.75 (d)	6.88 (d)	3.80 (OMe)	6.88 (d)	7.75 (d)		8.0	9.0			9.0				

[a] The absence of brackets after the δ value signifies superimposed resonances. [b] δ_{Et} 2.75 (q, CH_2) and 1.30 (t, CH_2). [c] δ_{CH_2} 4.60 (s). [d] C_5H_{11} δ 0.8, 1.30, and 2.75.

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EXPERIMENTAL

General purpose reagents were used throughout. Fresh samples of iron(III) oxide, aluminium(III) oxide, and titanium(IV) oxide were prepared by calcining the respective hydroxide at 700 °C for 1 h in air. I.r. spectra (KBr discs) and ^1H n.m.r. spectra (90 MHz) were recorded with Perkin-Elmer 457 and R32 instruments, respectively. Molecular weights were determined by mass spectrometry with an A.E.I. MS9 instrument; figures for compounds containing chlorine or bromine are calculated for the ^{35}Cl or ^{79}Br isotope.

General Acylation and Sulphonylation Procedure.—The substrate, reagent, and catalyst were mixed at room temperature, rapidly heated to 150 °C with agitation, and held at this temperature for 10 h. The product was cooled to 20 °C, the excess of substrate and unchanged reagent (if any) were removed by vacuum distillation (3—4 mmHg), and the relative amounts of each present in the distillate were estimated by ^1H n.m.r. analysis. The product was isolated in all cases by vacuum distillation (3—4 mmHg) of the remaining liquid. Pure samples for elemental analysis, mass spectrometry, and ^1H n.m.r. spectroscopy, were prepared by redistillation of liquid products over sodium carbonate, or recrystallisation of solid products from ethanol. Structures were assigned on the basis of ^1H n.m.r. spectra. The results are shown in Table 4.

The amount of hydrogen chloride evolved from reactions between 1,4-xylene (106 g, 1 mol) and benzoyl chloride (70 g, 0.5 mol) in the presence of metal oxides or iron or its compounds was estimated by passing a current of air through the reactor into a receiver containing water (600 ml) and a known amount of standard aqueous sodium hydroxide, with phenolphthalein as indicator. In view of the vigorous nature of many of the reactions, the procedure consisted of adding the reagent (at 25 °C) to the mixture of the hydrocarbon and catalyst (at 150 °C) over the shortest possible time (usually 1—2 min) and rapidly heating the resulting mixture to 150 °C.

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