Convenient Synthesis of Aromatic Acid Chlorides. The Reaction of Benzylidyne Chlorides with Hexamethyldisiloxane

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Summary Reactions of substituted benzylidyne chlorides with hexamethyldisiloxane in the presence of iron(III) chloride produce the corresponding substituted benzoyl chlorides in good yields.

ACID chlorides are usually synthesised by treating an acid with thionyl chloride or phosphorus pentachloride.[1] Newer methods[2] for the synthesis of aromatic acid chlorides have used the reactions of trichloromethylarenes with inorganic oxides such as titanium dioxide, vanadium pentoxide, sulphur oxides, or phosphorus pentoxide. However, these reactions generally require high temperatures (150—330 °C) and sometimes produce extremely corrosive hot inorganic chlorides. Therefore, a more convenient method which can be conducted under milder conditions is desirable. The reaction of a trichloromethylarene with an organosilicon oxide, hexamethyldisiloxane, is promising [equation (1)] and the putative product, αα-dichlorobenzyloxytrimethylsilane, would probably release

TABLE. Reactions of substituted benzylidyne chlorides with hexamethyldisiloxane in the presence of ferric chloride.[a]

Benzylidyne chloride	Temp./°C	Time/h	Product[b]	% Yield[c]
o-$ClC_6H_4CCl_3$	room temp.	1	*o*-ClC_6H_4COCl	79 (100)
p-$ClC_6H_4CCl_3$	50	0·5	*p*-ClC_6H_4COCl	84 (96)
2,4-$Cl_2C_6H_4CCl_3$ . .	60	0·4	2,4-$Cl_2C_6H_3COCl$	84 (91)
m-$Cl_3CC_6H_4CCl_3$[d] . .	70—80	1	*m*-$(COCl)_2C_6H_4$	74
p-$Cl_3CC_6H_4CCl_3$[d] . .	70—80	1	*p*-$(COCl)_2C_6H_4$	76

[a] Reactions were carried out by adding iron(III) chloride (5 mmol) to a mixture of the benzylidyne chloride (100 mmol) and hexamethyldisiloxane (100 mmol), unless otherwise specified. [b] All the products obtained were identified by comparing their physical properties with reported data. [c] G.l.c. yields are given in parentheses. [d] 2 equiv. of hexamethyldisiloxane were used.

a trimethylchlorosilane (β-elimination) to afford the corresponding aroyl chloride [equation (2)].

$$X\text{-}C_6H_4CCl_3 + (Me_3Si)_2O \longrightarrow [X\text{-}C_6H_4CCl_2OSiMe_3] + Me_3SiCl \qquad (1)$$

$$[X\text{-}C_6H_4CCl_2OSiMe_3] \xrightarrow[\beta\text{-elimination}]{} X\text{-}C_6H_4COCl + Me_3SiCl \qquad (2)$$

We found that benzylidyne chloride or substituted benzylidyne chlorides reacted at room temperature with an equimolar amount of hexamethyldisiloxane with iron(III) chloride as catalyst to give the corresponding substituted benzoyl chlorides together with trimethylchlorosilane.

Typically, to a mixture of benzylidyne chloride (136 mmol) and hexamethyldisiloxane (140 mmol) was added a catalytic amount of iron(III) chloride (6 mmol) and the mixture was stirred at room temperature. After 7 min, an exothermic reaction occurred and the temperature increased to 65 °C. Stirring was continued for 10 min and g.l.c. analysis of the resulting mixture showed that the benzylidyne chloride had been almost completely consumed and the yield of benzoyl chloride was estimated to be 93%. After removal of the low boiling material (trimethylchlorosilane), distillation under reduced pressure afforded 14·6 g of benzoyl chloride (b.p. 71—72 °C at 18 mmHg) in an isolated yield of 77%.[4]† Results for substituted benzylidyne chlorides are listed in the Table.

The present system has a distinct advantage over previous methods in that the reaction can be conducted under very mild conditions. Finally, the trimethylchlorosilane produced is readily hydrolysed to hexamethyldisiloxane which can be re-used [equation (3)].

$$2\,Me_3SiCl + H_2O \longrightarrow (Me_3Si)_2O + 2\,HCl \qquad (3)$$

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† Antimony pentachloride was also found to effect the reaction, but the yield was somewhat low. Other Lewis acids such as aluminium chloride and titanium chloride were unsatisfactory.

[1] 'Synthetic Organic Chemistry,' Wiley, New York, 1961, p. 546.
[2] R. C. Schreyer, *J. Amer. Chem. Soc.*, 1958, **80**, 3484; C. S. Rondestvedt, Jr., *J. Org. Chem.*, 1976, **41**, 3569; 3574; 3577.