

with strong Brønsted acids, though in poor yields<sup>[3]</sup>. However, the trifluoromethanesulfonic-carboxylic anhydrides obtainable from acyl chlorides and  $\text{CF}_3\text{SO}_3\text{H}$  do smoothly acylate aromatic compounds without addition of a catalyst<sup>[4]</sup>; in the course of the reaction, the sulfonic acid is set free again. Therefore,  $\text{CF}_3\text{SO}_3\text{H}$ -catalyzed acylation of

aromatic compounds with acyl chlorides appeared a possibility.

If a catalytic amount ( $\sim 1\%$ ) of  $\text{CF}_3\text{SO}_3\text{H}$  is added to a mixture of acyl chloride (1) and aromatic compound (2), hydrogen chloride is evolved more or less violently, depending on the reactivity of the reactants, and aromatic ketones (3) (Table 1) are formed.

In many cases carboxylic anhydrides may be made to react under similar conditions, but the yields are then slightly lower.

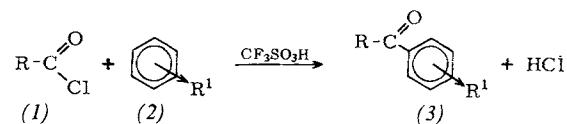


Table 1. Formation of aromatic ketones by catalytic Friedel-Crafts acylation.

(1), R	Reactants (2)	Conditions <i>T</i> (°C) <i>t</i> (h)	Product	Yield (%)	<i>o:p</i>
$\text{C}_6\text{H}_5$	Benzene	80	8.5	Benzophenone	14
$\text{C}_6\text{H}_5$	Chlorobenzene	132	5	2- and 4-Chlorobenzophenone	13 1:3
$\text{C}_6\text{H}_5$	Toluene	110	48	2- and 4-Methylbenzophenone	85 1:2
$\text{C}_6\text{H}_5$	<i>p</i> -Xylene	138	6	2,5-Dimethylbenzophenone	82
$p\text{-NO}_2\text{---C}_6\text{H}_4$	Benzene	80	4	4-Nitrobenzophenone	82
$(\text{CH}_3)_3\text{C}$	Anisole	154	12	<i>t</i> -Butyl <i>p</i> -methoxyphenyl ketone	54
$(\text{CH}_3)_2\text{CH}$	Anisole	154	0.2	Isopropyl <i>p</i> -methoxyphenyl ketone	46

### Catalytic Friedel-Crafts Acylation of Aromatic Compounds<sup>[1]</sup>

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For the synthesis of aryl ketones from aromatic compounds and acid chlorides or anhydrides at least one equivalent of Friedel-Crafts catalyst is required<sup>[2]</sup>. Highly activated arenes such as mesitylene or anisole may be acylated also

Trifluoromethanesulfonic-carboxylic anhydrides<sup>[4]</sup> formed as intermediates could be assumed to constitute the active acylating agent; on the other hand, the acylating potential of the acyl chlorides may also be increased sufficiently by protonation of the  $\text{C}=\text{O}$  group. We have therefore studied the catalytic efficiency of other strong Brønsted and Lewis acids. As shown in Table 2, catalytic acylation of arenes is possible in principle also with other acids; the yields, though, are of little preparative interest. Perchloric acid which has about the same acid strength as trifluoromethanesulfonic acid<sup>[5]</sup> is a considerably less effective catalyst. This finding supports our assumption that intermediate

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formation of mixed anhydrides is decisive for the catalytic influence of trifluoromethanesulfonic acid; a final decision, however, is not yet possible.

Table 2. Catalytic action of Brønsted and Lewis acids in the acylation of *p*-xylene by benzoyl chloride.

Catalyst	Amount (%)	Conditions <i>T</i> (°C)	<i>t</i> (h)	Yield (%)
CF <sub>3</sub> SO <sub>3</sub> H	1	138	6	82
FSO <sub>3</sub> H	1	138	6	20
<i>p</i> -CH <sub>3</sub> —C <sub>6</sub> H <sub>4</sub> —SO <sub>3</sub> H	1	138	6	31
H <sub>2</sub> SO <sub>4</sub>	1	138	6	28
HClO <sub>4</sub>	1	138	6	14
CF <sub>3</sub> COOH	2.6	138	10	21
HPOF <sub>2</sub>	3.1	138	10	4
AlCl <sub>3</sub>	2	138	15	26
SnCl <sub>4</sub>	2	138	15	30

*2,5-Dimethylbenzophenone:*

Benzoyl chloride (42 g) and *p*-xylene (95.5 g) are mixed and treated with trifluoromethanesulfonic acid (0.42 g), then heated for 6 h under reflux. After cooling, the reaction mixture is washed several times with water, dried over sodium sulfate and fractionated, yielding 82% (51.6 g) of 2,5-dimethylbenzophenone, b. p. 173–175 °C/12 torr. For recovery of the catalyst, the aqueous phases are neutralized with barium carbonate, and evaporated.

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