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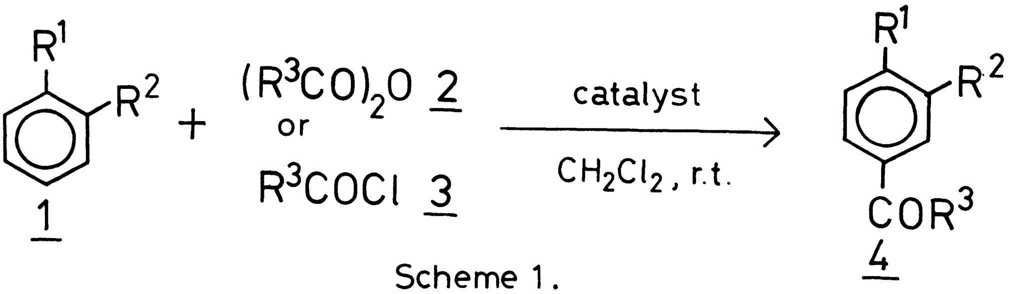
THE DIPHENYLBORYL HEXACHLOROANTIMONATE PROMOTED FRIEDEL-CRAFTS ACYLATION REACTION

Teruaki MUKAIYAMA, Hitoshi NAGAOKA, Masahiro OHSHIMA, and Masahiro MURAKAMI
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

In the presence of a catalytic amount of diphenylboryl hexachloroantimonate(Ph_2BSbCl_6), acid chlorides or acid anhydrides react smoothly with aromatic compounds such as anisole and veratrole to give the corresponding aromatic ketones in good yields under mild conditions. Diphenylboryl hexachloroantimonate also activates acyl enolates in the Friedel-Crafts acylation reaction to give the aromatic ketones in good yields under almost neutral conditions.

The Friedel-Crafts acylation reaction is a fundamental and useful reaction in organic synthesis and often employed in the industrial processes. However, the reaction generally requires an equimolar amount of activators such as $AlCl_3$ and BF_3.$^{1)}$ There have been some reports on the reactions promoted by a catalytic amount of activators such as activated iron sulfate,$^{2)}$ iron oxide,$^{3)}$ heteropoly acid,$^{4)}$ trifluoromethanesulfonic acid,$^{5)}$ but some of the reactions should be carried out at high temperature. In this communication, we wish to describe the Friedel-Crafts acylation reaction which proceeds under mild conditions by the promotion of a catalytic amount of Ph_2BSbCl_6.

In the previous papers, we reported that trityl perchlorate and diphenylboryl triflate (Ph_2BOTf) effectively activate acetals or carbonyl compounds, and various new and useful reactions have been developed.$^{6)}$ In the course of our investigations, we found that acid anhydrides (2) or acid chlorides (3) were activated by a catalytic amount of Ph_2BOTf to give the corresponding aromatic ketones (4) by the treatment with aromatic compounds (1) such as anisole and veratrole (Scheme 1).



Scheme 1.

After screening the diphenylboryl derivatives as promoters, it was found that, by the use of bis(p-methoxyphenyl)boryl hexachloroantimonate, the reaction proceeds smoothly at low temperature (r.t.) in CH_2Cl_2 to give the corresponding aromatic ketones ($\underline{4}$) in good yields as summarized in Table 1.

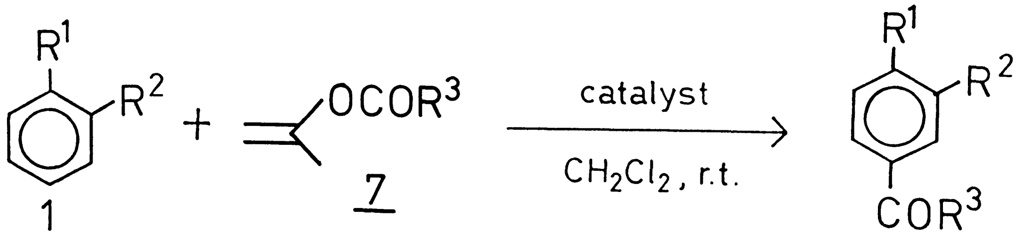
Table 1. The acylation reaction of aromatic compounds by acid chlorides or acid anhydrides

Entry	R^1	R^2	Catalyst	Acylating reagent	Conditions Temp/°C	Time/h	Yield of $\underline{4}$/%
1	OMe	OMe	Ph_2BOTf $\underline{5}$	$(PenCO)_2O$	r.t.	24	81
2	OMe	OMe	$\underline{5}$	BuCOCl	r.t.	24	52
3	OMe	H	$(p\text{-}MeOC_6H_4)_2BSbCl_6$ $\underline{6}$	$(PenCO)_2O$	r.t.	24	84
4	OMe	H	$\underline{6}$	MeCOCl	r.t.	24	53
5	OMe	H	$\underline{6}$	BuCOCl	r.t.	24	88
6	OMe	H	$\underline{6}$	t-BuCOCl	r.t.	24	70
7	OMe	H	$\underline{6}$	PhCOCl	r.t.	24	80
8	OMe	Me	$\underline{6}$	BuCOCl	r.t.	24	75

In the reaction mentioned above, the acyl groups were introduced regioselectively at the *para*-position of the substituents on the aromatic rings. And it should be pointed out that neither Ph_2BCl[7)] nor $SbCl_5$ was so effective in the present reaction, and it is assumed that the boron cation stabilized by two phenyl groups played an important role as an activator.

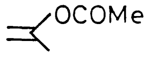
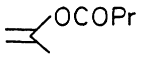
A typical procedure is described for the reaction of anisole with valeroyl chloride (entry 5); To a solution of $SbCl_5$ (0.12 mmol) in CH_2Cl_2 (1 ml) was added $(p\text{-}MeOC_6H_4)_2BCl$[8)] (0.14 mmol) in CH_2Cl_2(1.5 ml) at 0 °C under an argon atmosphere and the mixture was stirred for 1 h. Then a mixture of anisole (0.48 mmol) and valeroyl chloride (1.0 mmol) in CH_2Cl_2 (3 ml) was added at 0 °C and the reaction mixture was stirred for 24 h at room temperature. The reaction was quenched with aqueous $NaHCO_3$, and the resulting mixture was filtrated. Organic materials were extracted with CH_2Cl_2, and the combined extracts were dried with Na_2SO_4. After the solvent was evaporated, the residue was purified by preparative TLC to afford 1-(4-methoxyphenyl)-1-pentanone (0.42 mmol, 88%).

In the Friedel-Crafts acylation reaction using acid chlorides or acid anhydrides as acylating reagents, HCl or carboxylic acid is formed as the reaction proceeds, and the reaction mixture becomes fairly acidic. So it is more desirable to carry out the reaction under neutral conditions, and we next investigated the other acylating reagents which do not produce acidic substances as co-products. As the result, we found that according to the same procedure mentioned above, the acyl enolates ($\underline{7}$) are effectively activated by the use of a catalytic amount of Ph_2BSbCl_6 to afford the corresponding ketones ($\underline{4}$) in good yields at low temperature by treating with aromatic compounds ($\underline{1}$) such as anisole and veratrole (Scheme 2). The rerults are shown in Table 2.



Scheme 2.

Table 2. The acylation reaction of aromatic compounds by acyl enolates

Entry	R^1	R^2	Catalyst	Acylating reagent	Time/h	Yield of 4/%
1	OMe	OMe	Ph_2BSbCl_6 8	 9	24	71
2	OMe	OMe	8	 10	24	65
3	OMe	H	$(p\text{-}MeOC_6H_4)_2BSbCl_6$ 6	9	24	46
4	OMe	H	6	10	24	53
5	OMe	Me	6	9	24	52

In the present reaction, the co-product is only acetone and the reaction medium can be kept almost neutral throughout the reaction. Generally the Friedel-Crafts acylation reaction proceeds under strongly acidic conditions and there have been no report on the reaction using acyl enolates as acylating reagents. So the reaction catalyzed by Ph_2BSbCl_6 using acyl enolates as acylating reagents is a new and useful method for the synthesis of aromatic ketones under mild conditions.

Thus, it is noted that Ph_2BSbCl_6 effectively promotes the acylation reaction of aromatic compounds such as anisole and veratrole with acid chlorides or acid anhydrides to afford the corresponding ketones in good yields under mild conditions, and by the use of acyl enolates as acylating reagents, the reaction can be carried out under almost neutral conditions.

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8) $(p\text{-MeO-Ph})_2BCl$ was prepared from tetrakis(4-methoxyphenyl) stannane$^{9)}$ and BCl_3 in a similar manner to the preparation of Ph_2BCl.$^{7)}$ bp 128-133 °C/3 mmHg.

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