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A Novel Catalyst System, Antimony(V) Chloride-Lithium Perchlorate ($SbCl_5$-$LiClO_4$), in the Friedel-Crafts Acylation Reaction

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A novel catalyst system consisting of antimony(V) chloride ($SbCl_5$) and lithium perchlorate ($LiClO_4$) effectively promotes the Friedel-Crafts acylation reaction of aromatic compounds with acid anhydrides.

Although antimony(V) chloride ($SbCl_5$) is one of the most popular and easily available Lewis acids, its use in organic synthesis is rather limited compared with other Lewis acids such as $TiCl_4$, $SnCl_4$, BF_3OEt_2, etc.[1] Recently, we focused our attentions on unique characters of $SbCl_5$ when combined with other Lewis acids, and reported the catalytic Michael reaction,[2] the addition reaction of silyl nucleophiles with lactones[3] and the catalytic Beckmann[4] and pinacol[5] rearrangements. In this communication, we would like to report preliminary results on the catalytic Friedel-Crafts acylation reaction using a novel catalyst system, $SbCl_5$-lithium perchlorate ($LiClO_4$).

Results of the Friedel-Crafts acylation reaction of some aromatic compounds with acid anhydrides catalyzed by $SbCl_5$-$LiClO_4$ are listed in Table 1. Anisole, veratrole or 2-methylanisole smoothly reacts with acid anhydrides to give the corresponding acylated products in high yields. Mesitylene also works well. In the present reaction, acid anhydrides are better acylating reagents than acid chlorides. For example, anisole reacts with valeric anhydride to give the corresponding adduct in 85% yield (Table 1, entry 2), while 11% of the same product is obtained in the reaction using valeryl chloride under the same reaction conditions.[6]

A typical experimental procedure is described for the reaction of anisole with caproic anhydride; $SbCl_5$ (0.2 mmol) and $LiClO_4$ (5.0 mmol) were stirred for 1 h in dichloromethane (2.0 ml) at 0 °C. To this suspension was added a mixture of anisole (5.0 mmol) and caproic anhydride (10.0 mmol) in dichloromethane (2.0 ml) at this

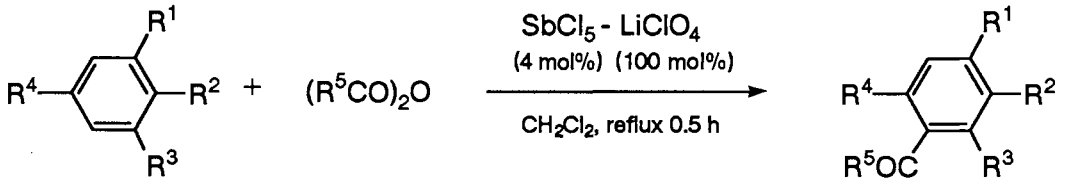


Table 1. The Friedel-Crafts Acylation Reaction Catalyzed by $SbCl_5$-$LiClO_4$

Entry	R^1	R^2	R^3	R^4	R^5	Yield / %
1	OMe	H	H	H	CH_3	89
2	OMe	H	H	H	C_4H_9	85
3	OMe	H	H	H	C_5H_{11}	92
4	OMe	OMe	H	H	C_5H_{11}	87
5	OMe	Me	H	H	C_5H_{11}	88
6	CH_3	H	CH_3	CH_3	CH_3	76 (95)[a]

a) 20 mol% of $SbCl_5$ was used.

temperature. The reaction mixture became red clear solution, and then was heated for 30 min under reflux. The red turned dark and the reaction was quenched with aq. sat. $NaHCO_3$. After usual work up, the crude product was purified on silica gel column chromatography to afford 1-(4-methoxyphenyl)-1-hexanone (85% yield).

Effect of the amount of $LiClO_4$ in the reaction of anisole with caproic anhydride was shown in Table 2.

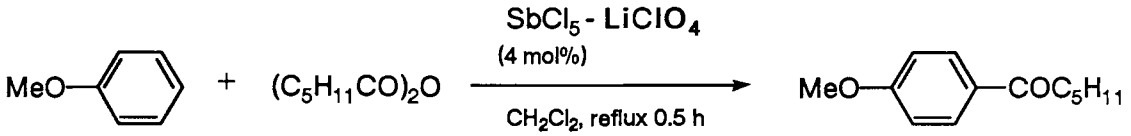


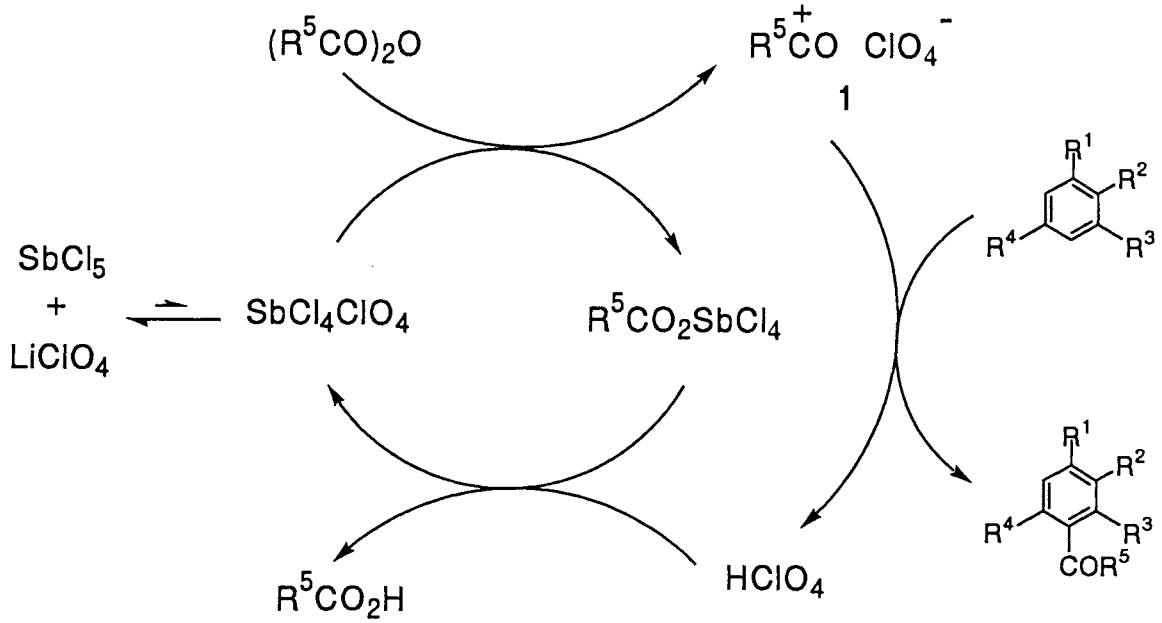
Table 2. Effect of $LiClO_4$ in the Reaction of Anisole with Caproic Anhydride [a]

$LiClO_4$ / mol%	0	10	50	100	200
Yield / %	48[b]	64	83	92	94

a) $LiClO_4$ alone (100 mol%) did not promote the present Friedel-Crafts acylation reaction.

b) 54% yield was obtained in the presence of 10 mol% of $SbCl_5$.

While the best yield was attained when 200 mol% of $LiClO_4$ was employed, the product was given in 92% yield when using one equivalent. Though the behavior of $LiClO_4$ is not clear at this stage,[7] it seems that $LiClO_4$ interacts with $SbCl_5$ to generate an active cationic species to accelerate the reaction, since the yields increased in accordance with the amount of $LiClO_4$. Lithium perchlorate alone is sparingly soluble in dichloromethane, however, the reaction medium becomes clear red solution immediately even in the presence of 200 mol% of $LiClO_4$. The reaction may proceed via the oxocarbenium perchlorate **1**,[8] but it should be noted that a catalytic amount of $SbCl_5$ is enough to complete the reactions in the present case. In addition, it was found that in the presence of 4 mol% of $SbCl_3(SbF_6)_2$ which is generated from $SbCl_5$ (4 mol%) and $AgSbF_6$ (8 mol%), anisole reacted with valeric anhydride to give the corresponding aromatic ketone in 57% yield.



Thus, a novel catalyst system, $SbCl_5$-$LiClO_4$, consisting of easily available and economical compounds, realizes the efficient Friedel-Crafts acylation reaction to provide aromatic ketones in high yields.[9] Further investigations to clarify the detailed mechanism including the behavior of $LiClO_4$ in this reaction as well as to develop other useful synthetic reactions by using this novel unique catalyst system are now in progress.

References

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3) K. Homma, H. Takenoshita, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **63**, 1898 (1990).

4) T. Harada and T. Mukaiyama, *Chem. Lett.*, **1991**, 1653.

5) T. Harada and T. Mukaiyama, *Chem. Lett.*, **1992**, 81.

6) When valeryl chloride was used as an acylating reagent, most of the starting material was recovered probably due to the incomplete regeneration of the catalyst.

7) Recently, Grieco et al. reported that Diels-Alder and some other reactions smoothly proceed in highly concentrated $LiClO_4$-Et_2O solution. P. A. Grieco, R. J. Nunes, and M. D. Gaul, *J. Am. Chem. Soc.*, **112**, 4595 (1990); P. A. Grieco, J. D. Clark, and C. T. Jagoe, *ibid.*, **113**, 5488 (1991); P. A. Grieco, R. J. Cooke, K. J. Henry, and J. M. VanderRoest, *Tetrahedron Lett.*, **32**, 4665 (1991). We had already reported that $LiClO_4$ is a quite effective additive in some glycosylation reactions. T. Mukaiyama, S. Kobayashi, and S. Shoda, *Chem. Lett.*, **1984**, 953; T. Mukaiyama, T. Shimpuku, T. Takashima, and S. Kobayashi, *ibid.*, **1989**, 145; T. Mukaiyama, K. Matsubara, and S. Suda, *ibid.*, **1991**, 981. See also, S. Winstein, S. Smith, and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959); Y. Pocker and R. F. Buchholz, *ibid.*, **92**, 2075 (1970).

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9) Recent reports on the catalytic Friedel-Crafts acylation reaction, see, T. Mukaiyama, T. Ohno, T. Nishimura, S. J. Han, and S. Kobayashi, *Chem. Lett.*, **1991**, 1059, and references cited therein. See also, F. Effenberger and D. Steegmüller, *Chem. Ber.*, **121**, 117 (1988).

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