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Magnesium bistrifluoromethanesulfonimide as an efficient catalyst for the hydroalkylation of aromatic olefins with 1,3-diketones under solvent-free conditions

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Abstract

An efficient magnesium bistrifluoromethanesulfonimide [$Mg(NTf_2)_2$] catalyzed hydroalkylation of aromatic olefins with 1,3-diketones under solvent-free conditions has been developed. The reactions proceed smoothly to give the desired products in good yields in short reaction times.

Keywords: Hydroalkylation; Aromatic olefins; 1,3-Diketones; Magnesium bistrifluoromethanesulfonimide

The hydroalkylation of alkenes with 1,3-dicarbonyl compounds is one of the most common methods for carbon–carbon bond formation in organic synthesis [1]. Generally, this transformation is carried out using alkyl halides in the presence of a stoichiometric amount of base [2]. Although this method works well even on large scale, it is often associated with many drawbacks including nonavailability of halogenated substrate, toxicity of halogenated substrates, the use of strong base and production of large amounts of salts as by-products. Therefore, the development of a practical and economical process for carbon–carbon bond formation between active methylene compounds and unmodified substrates is an important task. Recently, there are some reports on the direct hydroalkylation of alkenes with 1,3-dicarbonyl compounds in the presence of $AuCl_3$/AgOTf [3], $FeCl_3$ [4], I_2 [5], $Cu(OTf)_2$ [6], phosphotungstic acid [7], $SnBr_4$ [8] and $InCl_3$ [9]. Although each of the above methods has its own merit, some of these methods are limited by low yields and long reaction times. Therefore, the development of convenient and high yielding approaches to the hydroalkylation of 1,3-dicarbonyl compounds with alkenes is still desirable.

In recent years, metal bistrifluoromethanesulfonimides [$M(NTf_2)_n$] have been successfully used for the acetylation of phenols and alcohols [10], [2 + 2] cycloadditions of siloxy alkynes with carbonyl compounds [11], Friedel–Crafts acylation reactions [12], cycloisomerization of 1,6-dienes [13] and aminolysis of lactones with amines [14]. Previously, we have reported the use of $Eu(NTf_2)_3$ [15] and $Mg(NTf_2)_2$ [16] as efficient catalysts for the organic synthesis. $Mg(NTf_2)_2$ is commercially available, cheaper and not sensitive to air, and therefore, better suited for catalytic use. Following our interest in the catalytic uses of $M(NTf_2)_n$, we herein report an efficient method for the

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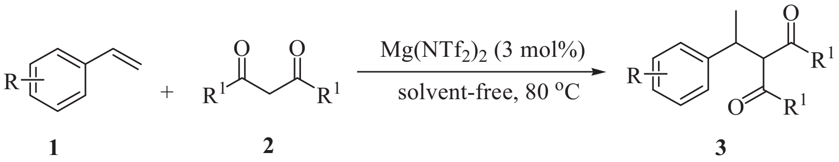


Scheme 1. Addition of 1,3-diketones to aromatic olefins catalyzed by $Mg(NTf_2)_2$.

hydroalkylation of aromatic olefins with 1,3-diketones in the presence 3 mol% of $Mg(NTf_2)_2$ under solvent-free conditions (Scheme 1).

In order to establish the optimum conditions for the hydroalkylation of aromatic olefins with 1,3-diketones, initially, using the reaction of acetylacetone with styrene as a model, we investigated the effect of the amount of catalyst on this reaction. It was found that 3 mol% of $Mg(NTf_2)_2$ (with respect to acetylacetone) is sufficient to promote reaction efficiently. In the absence of catalyst, the reaction did not proceed even after a long reaction time (22 h). Excess of $Mg(NTf_2)_2$ beyond this amount did not show any further increase in conversion and yield. Use of less than the required catalyst amount resulted in poor yield. Then, the effects of different solvents on the reaction were studied. Unsatisfactory yields and long reaction times were observed in the solvents (CH_2Cl_2, $CHCl_3$, CH_3CN, THF, DMF, DMSO, CH_3NO_2, H_2O, 1,2-dichloroethane and toluene) screened. The reaction exhibited the best results in terms of the yield and reaction time under solvent-free conditions. The reaction temperature has also a great influence on the reaction. We found that the reaction did not take place within 20 h when it was carried out at room temperature. Increasing the reaction temperature could remarkably enhance both reaction yield and rate. After the temperature was elevated to 80 °C, the reaction could be completed within 3 h and the product 3-(1-phenylethyl)- pentane-2,4-dione (**3a**) was isolated with high yield (91%). However, while increasing the temperature continuously, the yield has not obviously changed.

To demonstrate the generality of this method, we investigated the hydroalkylation of various aromatic olefins with 1,3-diketones in the presence 3 mol% of $Mg(NTf_2)_2$ under solvent-free conditions at 80 °C [17] and the results are summarized in Table 1. As shown in Table 1, in all cases, the reactions proceeded efficiently. Various aromatic olefins having methyl, *t*-butyl, methoxy, chloro and bromo underwent smooth hydroalkylation with 1,3-diketones to afford the corresponding products in high yields. In the case of 2-vinylnaphthalene, the corresponding products could also be obtained in high yields (Table 1, entries 7 and 12). Furthermore, both aliphatic (Table 1, entries 1–7) and aromatic (Table 1, entries 8–12) 1,3-diketones reacted smoothly with olefins under identical conditions.

Table 1
$Mg(NTf_2)_2$-catalyzed hydroalkylation reactions of aromatic olefins with 1,3-diketones.[a]

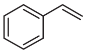
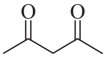
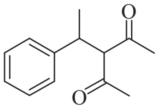
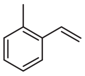
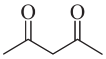
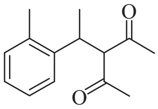
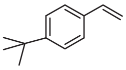
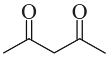
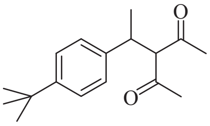
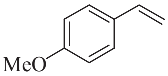
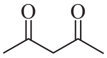
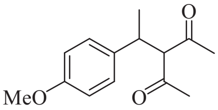
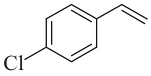
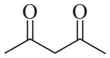
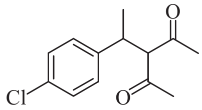
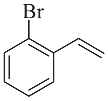
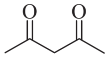
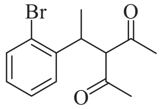
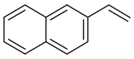
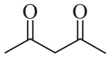
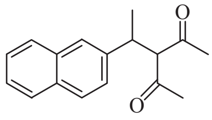
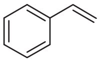
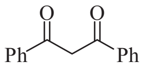
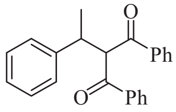
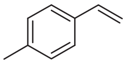
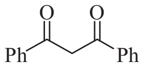
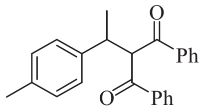
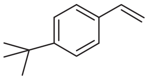
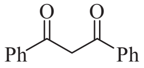
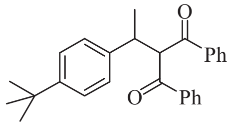
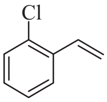
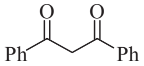
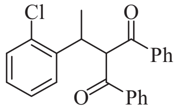
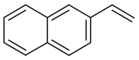
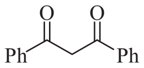
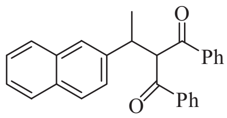
Entry	Aromatic olefin	1,3-Diketone	Product	Time (h)	Yield[b] (%)
1			 **3a**	3.0	91
2			 **3b**	2.5	93
3			 **3c**	2.0	96
4			 **3d**	4.5	82

Table 1 (*Continued*)

Entry	Aromatic olefin	1,3-Diketone	Product	Time (h)	Yield[b] (%)
5			 **3e**	3.5	88
6			 **3f**	4.0	84
7			 **3g**	3.0	91
8			 **3h**	3.0	90
9			 **3i**	2.5	94
10			 **3j**	3.0	92
11			 **3k**	3.0	88
12			 **3l**	4.0	89

[a] All the reactions were carried out with 3 mol% of $Mg(NTf_2)_2$ under solvent-free conditions at 80 °C.

[b] Isolated yields.

Table 2

Comparison of efficiency of various catalysts in the synthesis of 3 h.

Catalyst (mol%)	Conditions	Time (h)	Yield[a] (%)	Ref.
$AuCl_3$ (5)/AgOTf (15)	Room temperature/CH_2Cl_2	Overnight	93	[3]
$FeCl_3$ (30)	80 °C/1,2-dichloroethane	5.0	90	[4]
I_2 (10)	110 °C/toluene	5.5	88	[5]
$Cu(OTf)_2$ (15)	90 °C/dioxane	20.0	76	[6]
$SnBr_4$ (10)	50 °C/ionic liquid	6.0	60	[8]
$InCl_3$ (10)	100 °C/$MeNO_2$	15.0	65	[9]
$Mg(NTf_2)_2$ (3)	80 °C/solvent-free	3.0	90	This work

[a] Isolated yields.

In order to evaluate the efficiency of this work in comparison with previously reported procedures, synthesis of 1,3-diphenyl-2-(1-phenylethyl)propane-1,3-dione (3 h) was considered as a representative example. As shown in Table 2, the yield of our present method is better or comparable with others.

In conclusion, we have developed an efficient direct hydroalkylation reactions of aromatic olefins with 1,3-diketones catalyzed by $Mg(NTf_2)_2$. The reactions proceeded in high yields and avoided the use of toxic organic solvents. Simple workup, the use of a catalytic amount and commercially available catalyst, and short reaction time are the advantages of the present protocol. The properties of $Mg(NTf_2)_2$ such as stability, commercial availability, and high Lewis acidity, make $Mg(NTf_2)_2$ useful for catalytic applications [10].

Acknowledgments

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[17] General procedure: a mixture of aromatic olefin 1 (1.5 mmol), 1,3-diketone 2 (1.0 mmol) and $Mg(NTf_2)_2$ (3 mol%) was stirred at 80 °C. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and CH2Cl2 (2 × 10 mL) was added and the combined organic phases were washed with water. Removal of the solvent under reduced pressure afforded crude product 3, which was further purified by column chromatography.