The Catalytic Fries Rearrangement of Acyloxy Naphthalenes using Scandium Trifluoromethanesulfonate as a Catalyst

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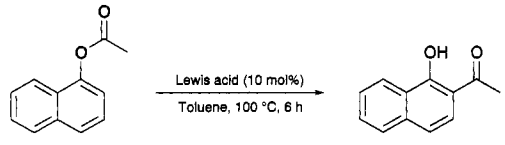
The catalytic Fries rearrangement of acyloxy naphthalenes proceeds smoothly using a small amount of scandium trifluoromethanesulfonate (5 mol%) to afford the corresponding hydroxynaphthyl ketones in high yields.

The Fries rearrangement is a synthetically useful reaction for the preparation of hydroxyarylketones not only in laboratories but also in industrial processes.[1] In particular, the Fries rearrangement of acyloxy naphthalenes affords the corresponding hydroxynaphthyl ketones, which can be converted to many alkyl and acyl naphthalene derivatives.[2–4] Recently, these were reported to be versatile intermediates for the synthesis of biologically active naphthoquinone derivatives.[3] Moreover, in the field of liquid crystals (LC), naphthalenes containing LC polymers or low molecular mass mesogens have attracted much attention owing to their unique properties.[4] Although the Fries rearrangement has generally been carried out using $AlCl_3$ as a promoter, more than a stoichiometric amount of the Lewis acid is required because most Lewis acids are deactivated by the free hydroxy groups of the products.† On the other hand, a photo-Fries rearrangement has also been developed to overcome the disadvantages of the Lewis acid-promoted reactions.[3,5] However, control of the reaction courses as well as application to large scale synthesis still remain as problems. In this paper, we describe the catalytic Fries rearrangement of acyloxy naphthalenes using scandium trifluoromethanesulfonate [scandium triflate, $Sc(OTf)_3$] as a catalyst.

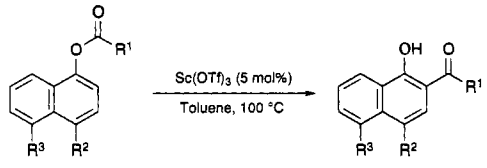
Table 1 Effects of Lewis acids[a]



Entry	Lewis acid	Yield (%)
1	$AlCl_3$	0
2	$TiCl_4$	7
3	$SnCl_4$	Trace
4	$BF_3{\cdot}OEt_2$	Trace
5	$Yb(OTf)_3$	2
6	$Sc(OTf)_3$	75 (85)[b]
7	$AlCl_3$ (140 mol%)	61[c]
	(Photo)	38[d]

[a] The reaction was carried out in 1 mol dm^{-3} toluene. [b] In 0.5 mol dm^{-3} toluene using 5 mol% $Sc(OTf)_3$. [c] Ref. 2a. [d] Ref. 3.

Table 2 $Sc(OTf)_3$-catalysed Fries rearrangement of 1-acyloxynaphthalenes



Entry	R^1	R^2	R^3	Yield (%)
1	Me	H	H	85
2	Me	OMe	H	80
3	Me	H	OMe	58
4	Et	H	H	89
5	C_5H_{11}	H	H	85
6	c-C_6H_{11}	H	H	78

We have recently found that $Sc(OTf)_3$ is a stable Lewis acid in water and effectively catalyzes Diels–Alder, aldol, Michael, and allylation reactions.[6] We also found that catalytic Friedel–Crafts acylation reactions proceed smoothly using $Sc(OTf)_3$ as a catalyst.[7] Through these investigations, it was found that $Sc(OTf)_3$ is not trapped by the carbonyl oxygens of aromatic ketones as $AlCl_3$ is, and that free hydroxy and carboxylic groups do not decrease the Lewis acidity. Bearing this information in mind, we examined the Fries rearrangement of acyloxy naphthalenes using a catalytic amount of $Sc(OTf)_3$.

First, a 1 mol dm^{-3} toluene solution of 1-naphthyl acetate was treated with 10 mol% of $Sc(OTf)_3$ at 100 °C. After 6 h, 1-hydroxy-2-acetonaphthone was obtained in a 75% yield. The yield was improved to 85% when the reaction was carried out at a lower concentration (0.5 mol dm^{-3}). It is noted that the reaction proceeded sluggishly when catalytic amounts of typical Lewis acids were used, and that the yield was much higher than that in the stoichiometric $AlCl_3$-promoted reaction or that in the photo reaction (Table 1). The Fries rearrangements of several acyloxy naphthalenes are shown in Table 2. In every case, the reactions proceeded smoothly using a catalytic amount of $Sc(OTf)_3$ to afford the corresponding hydroxynaphthyl ketones in good yields.

A typical experimental procedure is described for the Fries rearrangement of 1-naphthyl acetate: To $Sc(OTf)_3$ (0.05 mmol, 5 mol%) and 1-naphthyl acetate (1.0 mmol) was added toluene (2.0 ml) at room temperature. The mixture was stirred for 6 h at 100 °C and was then cooled to room temperature. Water was added to quench the reaction and CH_2Cl_2 was then added. After separation of the organic layer, the aqueous layer was extracted (CH_2Cl_2 twice) and the combined organic layers were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the crude product was chromatographed on silica gel to afford 1-hydroxy-2-acetonaphthone (85% yield).

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Footnote

† The Fries rearrangement is promoted by some protic acids such as hydrofluoric, perchloric, polyphosphoric and sulfonic acids.[1]

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