Pergamon

Tetrahedron Letters 40 (1999) 3161-3164

TETRAHEDRON
LETTERS

New Synthesis and Reactions of [Sm(OTf)$_2$(DME)$_2$], a Salt-Free Samarium(II) Triflate

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Received 4 February 1999; accepted 21 February 1999

Abstract

A new, simple and high-yield synthesis of a salt-free samarium(II) triflate, [Sm(OTf)$_2$(DME)$_2$] is described. In stoichiometric amounts this derivative mediates typical samarium (II) coupling reactions such as pinacolisation, dimerisation of imines and Barbier-type reactions. It can also acts as a precatalyst for Mukaiyama aldol and Michael reactions and Diels-Alder reactions. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords : Divalent samarium, Coupling reactions, Catalysis, Lewis acid .

Although many samarium (II) compounds have been isolated in the past years, few of them have found widespread applications in organic chemistry. Apart from the ubiquitous SmI$_2$ [1], which is now commercially available, SmBr$_2$ [2] and SmCp$_2$ [3] have also been employed. Recently, samarium (II) triflates, prepared by reduction of Sm(OTf)$_3$ with organometallic compounds have appeared in the literature [4-5]. These salt-containing species were formulated as Sm(OTf)$_2$ and used *in situ* but not isolated. In a very recent paper, salt-free [Sm(OTf)$_2$(solv)$_x$] (solv = CH$_3$CN, THF) have been unambiguously prepared and the X-Ray structure of [Sm(OTf)$_2$(THF)$_{1.5}$] determined [6]. The synthesis involved the reaction of metallic samarium with 1,5-dithioniabicyclooctane bis(triflate). Since this reagent is not easily prepared [7], we investigated a simpler synthesis of salt-free Sm(OTf)$_2$ involving the reduction of commercially available Sm(OTf)$_3$ by Sm metal [8]. We wish to report on this and on a preliminary assessment of the synthetic applications of this reagent in organic chemistry.

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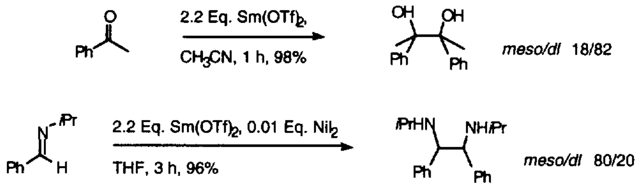
0040-4039/99/$ - see front matter © 1999 Published by Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(99)00417-7

We found that activation of samarium metal with a catalytic amount of mercury, and the use of 1,2-dimethoxyethane (DME) as a solvent, ensured a reproducible and high-yielding synthesis of $[Sm(OTf)_2(DME)_2]$ from $Sm(OTf)_3$ and Sm metal .

$$2[Sm(OTf)_3] + Sm \xrightarrow{\text{Hg cat., DME}} 3[Sm(OTf)_2(DME)_2]$$

Reduction of $Sm(OTf)_3$ by activated samarium also occurred in THF, but was less consistent because of occasional precipitation of $[Sm_4(OTf)_9(THF)_7]$ (characterized by X-Ray crystallography) [9] in which Sm is present both in the +III (for one atom) and the + II (for 3 atoms) oxidation states. The use of unactivated samarium was generally unsuccessful. $[Sm(OTf)_2(DME)_2]$ is soluble in CH_2Cl_2, THF and acetonitrile, and, like SmI_2, is very air- and water-sensitive and should be manipulated in a dry, inert atmosphere such as N_2 or Ar[1].

We have screened the reactivity of $[Sm(OTf)_2(DME)_2]$ as a stoichiometric reagent in various coupling reactions. Pinacolisation of acetophenone in acetonitrile realized in similar conditions to those of Tani, [6] gave similar yields and diatereoselectivities, confirming that both methods of synthesis afforded the same Sm(II) derivative. Dimerisation of imines by samarium diiodide requires more drastic conditions [10] and we have recently shown that the use of NiI_2 as an additive greatly enhances the reaction rate [11]. The coupling reaction of imines mediated by $[Sm(OTf)_2(DME)_2]$ in the presence of 1% mol NiI_2 yielded diamines with a higher *meso/dl* ratio than that observed with SmI_2.



We found $[Sm(OTf)_2(DME)_2]$ mediated Barbier-type reactions, occured in high yields, in the presence of additives such as HMPA or NiI_2 whereas the $[Sm(OTf)_2(DME)_2]$ mediated reaction of an alkyl iodide with acetophenone, according to the Grignard procedure, led to a complex mixture of products. In contrast, under the same conditions, Fukuzawa [4] reported that with his Sm(II) triflate complex, which contains lithium salts, the Barbier coupling did not occur and the major products formed were diols resulting of the pinacolisation of the ketones,

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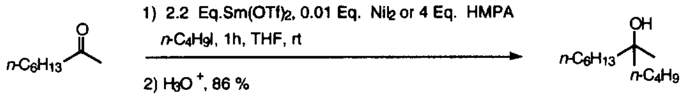
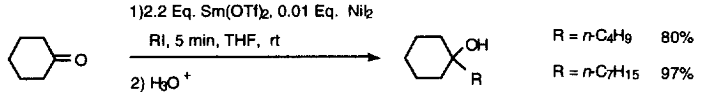
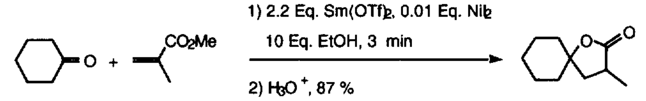
[1] A typical procedure is as follows : In a 500 mL Schlenk flask attached to a vacuum line and cooled at -78°C in a dry ice-acetone bath, dry DME (120 mL) was condensed by vacuum distillation onto a mixture of $Sm(OTf)_3$ (11.95 g, 20 mMole), Sm chips (1.82 g, 11.3 mMole) and Hg (2 drops, 230 mg). The flask was then disconnected from the vacuum line and the resulting thick slurry was stirred at room temperature under static vacuum. The reaction started within 1h (a red colour appeared) and was complete after 48h. The dark purplish-black reaction mixture was then evaporated to dryness, extracted into THF (250 mL) (in a glove box under Ar), filtered from the metallic residues and the filtrate was evaporated to dryness. The residue was suspended in DME (100 mL), stirred at 40°C for 1h, then cooled to 0°C and filtered. The precipitate was dried under vacuum for 3h. $[Sm(OTf)_2(DME)_2]$ (17.2 g, 27.3 mMole, 91%) was thus obtained as a purple powder. The exact DME content was determined by standard iodometric titration.

whereas under the conditions of the Grignard procedure formation of the expected tertiary alcohol was observed.

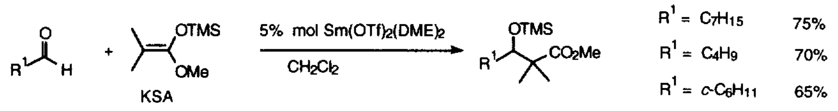




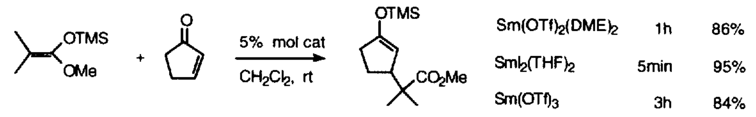
The coupling reaction of cyclohexanone with methyl methacrylate mediated by samarium bis triflate in the presence of NiI_2 and an excess of ethanol readily afforded the lactone in high yield, a reaction which has not been described with the Fukuzawa's complex [4].



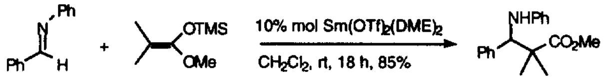
Trivalent lanthanide triflates can act as Lewis acid catalysts for a wide range of reactions [12], for example Mukaiyama aldolisation, Diels-Alder reactions, or the addition of enoxysilanes onto imines. We have previously reported that $[SmI_2(THF)_2]$ is a precatalyst for these reactions [13-14] and we have now tried to evaluate the catalytic properties of $[Sm(OTf)_2(DME)_2]$, in solution in dichloromethane, as a Lewis acid. At room temperature, $[Sm(OTf)_2(DME)_2]$ (5% mol) catalyzed the formation of aldol silyl ethers from aldehydes and a dimethylketene silyl acetal (KSA) in a Mukaiyama aldol-type reaction. Aldol silyl ethers were also obtained with $[SmI_2(THF)_2]$ as a precatalyst, but only at low temperature, as at room temperature the silyl enol ethers formed by the competing enolisation of aldehydes are the only products. With $[Sm(OTf)_2(DME)_2]$ as a catalyst, the rate of the enolisation reaction is slow for aldehydes compared to that of the aldol reaction and the SmI_2-catalyzed enolisation reaction. In the case of a ketone, for example the reaction of 4-*t*-Bu-cyclohexanone with KSA at room temperature, catalysis by $[Sm(OTf)_2(DME)_2]$ furnished a mixture of products, the condensation product and the 4-*t*-Bu-trimethysilyloxycyclohexene. The latter was the only product obtained using $[SmI_2(THF)_2]$ as a catalyst.

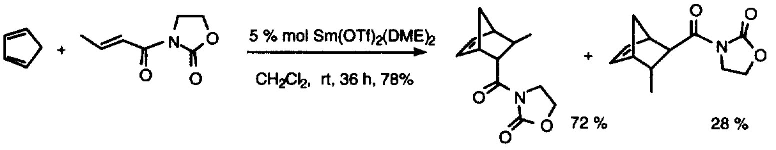


$[Sm(OTf)_2(DME)_2]$, $[SmI_2(THF)_2]$ and $Sm(OTf)_3$ were all found to catalyze Michael additions of KSA to cyclopenten-2-one affording an enoxysilane at room temperature. $[SmI_2(THF)_2]$ is the most active catalyst, as indicated by the reaction conditions.



$[Sm(OTf)_2(DME)_2]$ and $[SmI_2(THF)_2]$ catalyze efficiently the addition of an imine to KSA, and the Diels-Alder reaction of cyclopentadiene and crotonoyl oxazolidinone. Both Sm(II) reagents allow the clean formation of the addition products, at room temperature, with similar rates.





In all experiments the purple colour of $[Sm(OTf)_2(DME)_2]$ disappeared and the reaction mixture became colourless after introduction of the reactants. This is indicative of a trivalent active species. Thus, $[Sm(OTf)_2(DME)_2]$ is the precursor of trivalent catalysts, efficient in several reactions such as Diels-Alder reactions and aldol-type reactions.

In conclusion, we have found a simple high-yield synthesis of $[Sm(OTf)_2(DME)_2]$ and have shown in preliminary experiments that this reagent can be an alternative to other divalent Sm reagents.

Acknowledgments: We thank the Université Paris-Sud, the CNRS, the Ecole Polytechnique for their financial support, and the MENESR for fellowships (to N.G. and F.M.).

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