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Samarium Diiodide in Tetrahydropyran : Preparation and some Reactions in Organic Chemistry.

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Abstract : SmI_2 could be readily prepared in tetrahydropyran (THP) from samarium and 1,2-diiodoethane. Reducing properties were studied, showing marked differences compared to the classical SmI_2/THF system.

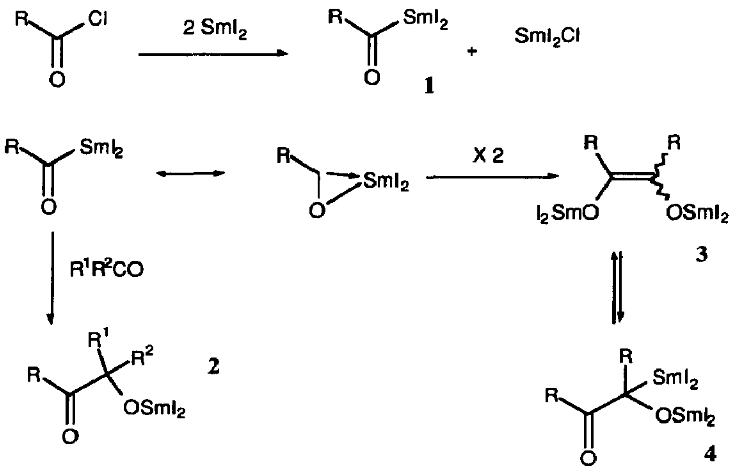
We reported in 1977 the synthesis of SmI_2 in tetrahydrofuran and its use in organic chemistry.[2] This reagent displayed a variety of reactions and proved very useful in organic synthesis [3]. However the presence of THF is sometimes detrimental to some reactions because of its hydrogen donor properties towards radicals intermediates or because of some ring opening reactions, especially by acid chlorides. There are few cases where SmI_2 has been prepared in another solvent for avoiding any traces of THF. Preparation of SmI_2 in acetonitrile has been briefly reported [4]. A tedious preparation of SmI_2 in a mixture of benzene and HMPA has been published [5]. We could not synthesize SmI_2 (from samarium and diiodoethane) in ethers such as diethyl ether, terbutyl methyl ether or dioxane. We wish to describe the successful preparation of samarium diiodide in tetrahydropyran (THP) and the first results concerning the reducing properties of this reagent compared to the reactions occuring in THF under the same experimental conditions.

The preparation of SmI_2 in THP occurs at room temperature from reaction between samarium and 1,2-diiodoethane, titrations and U.V.-visible spectra agree with quantitative formation of SmI_2 [6].

The reactivity of SmI_2 in THP towards *acid chlorides* R(CO)Cl has been explored at first because various limitations are encountered in THF. The major drawback is the formation of the iodo ester $R(CO)O(CH_2)_4I$ arising from ring opening of THF [8].

The mechanism of the reaction of acid chlorides with aldehydes or ketones mediated by SmI_2 in THF has been explored (scheme 1). It proceeds through formation of an acyl samarium species **1** which must be in situ trapped by aldehyde or ketone to lead to α-ketolate **2**, otherwise it dimerizes to an enediolate **3** whatever the temperature is [8, 9].

Scheme 1 : mechanism of reactions of acid chlorides with SmI_2.



Beneficial aspects of the use of THP, is first the complete absence of by-products arising from ring opening of the solvent and second the possibility to carry out the reductive coupling of acid chlorides in a sequential manner (Table 1). This last reaction is impossible in THF, the α-ketols **II** immediately form.

The sequential reaction is particularly interesting because it broadens the synthetic scope of production of α-ketols **I**, allowing to use aldehydes (which otherwise are readily transformed into pinacols by diiodosamarium itself) [10]. The main limitation of the sequential method in THP is the need to use acid chlorides with a branched α-carbon. The two steps procedure confirms that an organosamarium has been stored in the THP solution. Furthermore if 1-adamantyl carbonylchloride is reacted with SmI_2/THP and then with D_2O, a mixture of α-ketol and 1-adamantane carboxaldehyde is obtained (Scheme 2). The products are quantitatively C-deuterated. This result also strongly supports the transient formation of an acyl samarium **1**.

Scheme 2 : trapping of samarium acyl anion 1 (R=adamantyl), with D_2O.

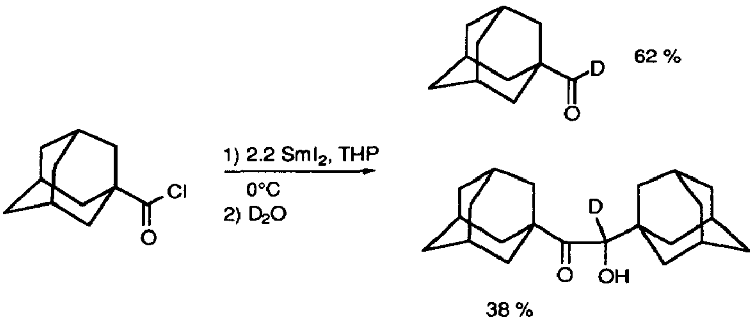
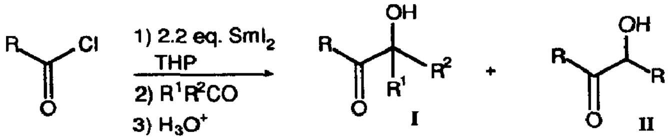


Table 1 a)

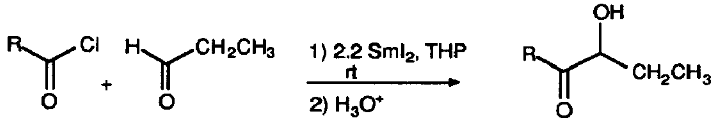


R	R^1, R^2	t°C	yield % I ; gc, (isolated)	yield % II ; gc, (isolated)
1-methylcyclohexyl	H,C_2H_5 b)	-18	>95	traces
1-methylcyclohexyl	H, C_2H_5	0	>95 (67)	traces
1-methylcyclohexyl	H, C_2H_5	25	55	45
1-methylcyclohexyl	CH_3, C_2H_5	0	94 (71)	traces
1-methylcyclohexyl	H, C_6H_5	0	>95 (71)	traces
1-methylcyclohexyl	$(CH_2)_5$ c)	0	80 (56)	traces
1-adamantyl	CH_3, C_2H_5 c)	-18	>95 (80)	traces
1-adamantyl	CH_3, C_2H_5 c)	0	84	16
n-octyl	H, C_2H_5	-18	0	80 d)
cyclohexyl	H, C_2H_5	-18	0	90 (80) d)

a) A representative example is as follow : to 12 mmol of SmI_2 suspended in 120 mL of THP in a Schlenck tube under argon, are slowly added at the temperature quoted in the table, 5.4 mmol of the acid chloride in 20 mL of THP. The mixture turns brown and is kept for 10 min. The carbonyl compound (6 mmol in 5 mL of THP) is then added. The solution turns yellow within 5 min. Workup is as described in [11] b) If the amount of aldehyde is in excess by respect to acid chloride, ketol I is mixed with the isomeric ketol probably because of a samarium MPV/O reaction [12]. c) In order to avoid deshydroxylation of α-ketol [9] the ratio SmI_2/ ketone is 2.05. d) A minor by-product is the ester R(CO)CH(R)O(CO)R which arises from the reaction of the samarium ketolate 4 with acid chloride.

With cyclohexanoyl chloride and n-nonanoyl chloride, even at -18°C self coupling of the acylsamarium occurs. Nevertheless the coupling between these acid chlorides and propanal can be performed in Barbier conditions as well as the coupling of 1-adamantanecarbonyl chloride with propanal [13] (Scheme 3).

Scheme 3 : coupling of acid chlorides with propanal mediated by SmI_2/THP.



R=cyclohexyl, yield % = 86
R=1-adamantyl, yield % = 83
R=n-octyl, yield % = 80

In conclusion the preparation of SmI_2 in THP is quite easy. This reagent (in 10^{-2} M solutions or as slurry) can be conveniently handle and stored. Reactions involving acid chlorides are cleaner in THP than in THF, side reactions due to ring opening of the solvent are avoided. One benefit of THP by respect to THF is the stabilization of acyl samarium **1** (when R is a branched group) allowing to store these species in solution around 0°C. Nevertheless they are reactive towards electrophiles such as aldehydes or ketones. The scope of reactivity of SmI_2 in THP towards various organic substrates is under investigation.

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6 In a Schlenck tube under argon, 150 mg (1 mmol) of samarium powder, 282 mg (1 mmol) of 1,2-diiodoethane and 1 mL of THP are mixed; after a short induction period, a slightly exothermal reaction takes place and the mixture turns blue-violet, a slurry of SmI_2 is obtained, amount of THP required for experiment is then added.
The U.V.-visible spectrum of SmI_2 in THP is very similar to the spectrum in THF [7].
$[SmI_2] = 10^{-2}$ M ; quartz cells 1 mm ; λ_{max} in nm, (ε_{max} in $dm^3. mol^{-1}. cm^{-1}$) : 606, (462) ; 543, (495) ; 407, (580) ; 347, (873) ; 336, (796)· After air oxidation the solution shows only one band at 358 nm.

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13 The mixture of acid chloride and aldehyde must be slowly added to SmI_2/THP in order to avoid reaction of ketolate **2** with acid chloride, leading to ester.

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