

THE EVALUATION OF DICYCLOPENTADIENYLSAMARIUM AS A REAGENT IN ORGANIC SYNTHESIS *

J.L. NAMY, J. COLLIN, J. ZHANG and H.B. KAGAN*

Laboratoire de Synthèse Asymétrique, UA CNRS No. 255, Université Paris-Sud, 91405-Orsay (France)

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Summary

SmCp_2 , which is easily prepared from SmI_2 , has been screened as a reducing agent for organic chemistry. In particular, SmCp_2 promotes the pseudo-Barbier reaction between carbonyl compounds (aldehydes and ketones) and aliphatic or allylic halides more efficiently than does SmI_2 .

Introduction

In 1977, we described the facile preparation of SmI_2 and some of its reducing properties towards organic compounds [1]. Since then, many aspects of the reactions of SmI_2 with organic [1–4] and organometallic compounds [5–7] have been examined. The chemistry of lanthanides has been widely investigated using cyclopentadienyl or substituted cyclopentadienyl groups as ligands [8–10] but information on the organometallic chemistry of divalent samarium analogues has been obtained only for $\text{Sm}(\text{Me}_5\text{C}_5)_2$, which is a soluble species in organic solvents [8–10]. We wish to report here that the readily available dicyclopentadienylsamarium [7], although insoluble in most organic solvents, promotes several types of organic transformations. The scope of these reactions is discussed, and compared with those mediated by SmI_2 .

Results and discussion

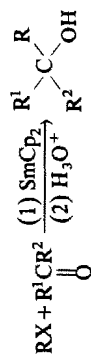
Preparation of SmCp_2

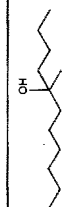

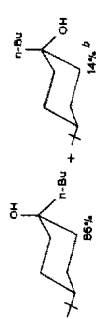



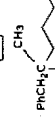

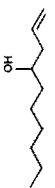

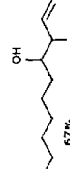
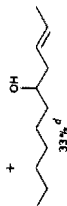
SmCp_2 is readily obtained by the reaction of SmI_2 with NaCp [7] in THF under argon at room temperature; SmCp_2 separates as a red powder, which can be stored in an inert atmosphere. Suspensions of freshly prepared SmCp_2 were used for the various reactions described below.


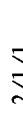




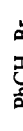


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* Dedicated to Professor Jean Tiroufflet on the occasion of his retirement.

TABLE 1
 REACTIONS OF HALIDES AND CARBONYL DERIVATIVES WITH SmCp₂



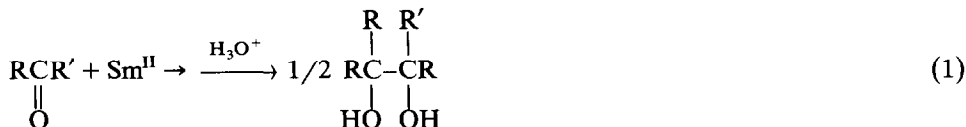
Entry	RX	R ¹	R ²	Products	Molar ratio Cp ₂ Sm/RX/R ¹ CR ²	Yield ^a
1	<i>n</i> -BuI	C ₆ H ₁₃	CH ₃		2/1/1	69
2	<i>n</i> -BuI			 +  (14% ^b)	2/1/1	65 ^b
3	<i>n</i> -BuI	CH ₃	CH ₂ CH ₂ COOEt		3/1.5/1	89 ^c
4	<i>i</i> -PrI	CH ₃	CH ₂ CH ₂ COOEt		3/1.5/1	76 ^c
5	<i>n</i> -BuI	CH ₃	CH ₂ Ph		3/1.25/1	58 ^d
6		C ₆ H ₁₃	H		3/1.25/1	86
7		C ₆ H ₁₃	H	 (67%) +  (33% ^d)	3/1.25/1	84 ^e

8	PhCH ₂ Br	C ₆ H ₁₃	H		2/1/1	60
9	BrCH ₂ COOEt	C ₆ H ₁₃	H		3/1.25/1	81
10	BrCH ₂ COOEt	<i>t</i> -Bu	H		3/1.25/1	80
11	CH ₃ I	C ₆ H ₁₃	H		3/2/1	18 ^f
12	<i>i</i> -PrI	C ₆ H ₁₃	H		3/1/1	50
13	<i>n</i> -BuI	C ₆ H ₁₃	H		2/1/1	39
14	<i>n</i> -BuI	C ₆ H ₁₃	H		4/1/1	59
15	<i>n</i> -BuBr	C ₆ H ₁₃	H		3/1/1	19
16	<i>n</i> -C ₇ H ₁₅ I	C ₆ H ₁₃	H		3/1/1	35
17	<i>n</i> -C ₁₂ H ₂₅ I	C ₆ H ₁₃	H		3/1/1	71
18	<i>n</i> -BuI	<i>t</i> -Bu	H		2/1/1	35

^a Isolated yields. Reaction performed at room temperature in THF. ^b Epimers were identified with GC by comparison with reference samples. ^c Contaminated with 10% ethyl levulinate. ^d After chromatography on a silica column a yield of 85% of a product contaminated with 10% methyl benzyl ketone was obtained. Further purification on alumina column was necessary. ^e The isomeric alcohols were separated by chromatography on a silica column. ^f Diols (C₈H₁₃CH(OH)CH(OH)C₆H₁₃) were also isolated (20% yield).

The major reactions of SmCp₂

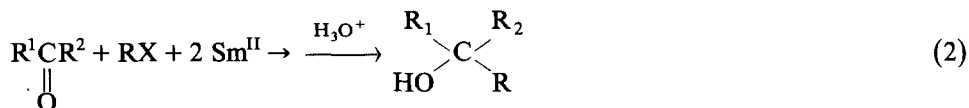
Most of the transformations induced by SmI₂ are initiated by a one-electron transfer to an organic substrate followed by several steps involving radical intermediates and for further electron transfer reactions [11]. It was thus interesting to compare the behaviour of SmI₂ and SmCp₂ in a typical reaction, e.g. pinacol formation from benzaldehyde or acetophenone (R = H or Me, reaction 1).



A suspension of SmCp₂ in THF solubilized rapidly at room temperature on addition of 1 mol eq. of the carbonyl compound. After hydrolysis, the pinacol was isolated in almost quantitative yield, as previously described for the reaction with SmI₂ [12].

Several alkyl iodides were readily reduced to the corresponding alkanes with 2 mol eq. of SmCp₂ at room temperature.

One of the most interesting properties of SmI₂ is that it promotes a pseudo-Barbier reaction (see eq. 2). With ketones the yields are excellent if the reactions are performed in THF under reflux.



Reaction with aldehydes often leads to a mixture of products because the intermediate samarium alcoholate and SmI₂ behave as catalysts for the Meerwein-Ponndorf-Verley-Oppenauer (MPV/O) reaction [13,19]. We thus investigated the use of SmCp₂ in the pseudo-Barbier reaction in the presence of either ketones or aldehydes and the results are listed in Table 1.

A THF solution of organic halide and carbonyl compound was added to a suspension of SmCp₂ in the same solvent. Usually dissolution occurred within 1 h at room temperature, the yellow colour of Sm^{III} indicating the end point. After work-up [11] the crude product was purified by flash chromatography. Tertiary alcohols are formed in good yield from various ketones and an alkyl halide, namely butyl iodide (entries 1-3). With ethyl levulinate (entries 3-4) lactones were obtained in high yield by cyclization of the intermediate samarium alcoholate [14,15].

These aspects of the chemistry of SmCp₂ were not further investigated because SmI₂ also gives very good results [11]. It should be noted, however, that the experimental conditions are much milder (room temperature) when SmCp₂ is used. The same limitations were found for SmCp₂ and SmI₂: an aromatic ketone such as acetophenone mainly gives the pinacol, while a highly enolizable ketone (β -tetralone, Dieckmann ester) undergoes enolization rather than the pseudo-Barbier reaction.

This pseudo-Barbier reaction was then attempted with aldehydes because, except when reactive halides were used (allyl or benzyl halides), very low yields of alcohols were obtained when SmI₂ was used [12]. The reaction of C₆H₁₃CHO with allyl iodide, crotyl bromide benzyl bromide, or ethyl bromoacetate took place cleanly in the presence of SmCp₂ (entries 6-9, Table 1). This parallels some of the results

obtained with SmI_2 . However SmCp_2 is also able to promote the reaction between aliphatic iodides and aldehydes (entries 11–14, 16–18, Table 1); the by-products are pinacols. The best results were obtained with a reagent ratio of $\text{Cp}_2\text{Sm}/\text{RX}/\text{aldehyde} = 3/1/1$ for aliphatic iodides and $3/1.25/1$ for more reactive halides. The reaction occurs under very mild conditions, tolerates the ester function (entries 9 and 10), and seems to be applicable to a wide range of aliphatic aldehydes (entries 6–18). However aromatic aldehydes or α,β -unsaturated aldehydes undergo pinacol formation faster than the pseudo-Barbier reaction in presence of butyl iodide [16].

In conclusion, SmCp_2 is more effective than SmI_2 in promoting the pseudo-Barbier reaction between aliphatic aldehydes and various organic halides, probably because the SmCp_2 does not catalyse undesirable side reactions such as the MPV/O and Tischenko reactions [18].

Experimental

Apparatus

Proton magnetic resonance spectra (^1H NMR) were recorded with a Perkin–Elmer Model R 32 spectrometer at 90 MHz or with a Bruker 250 MHz instrument. Chemical shifts in CDCl_3 are reported in parts per million from Me_4Si as an internal standard. Mass spectra were obtained with a GC-MS Ribermag R 10-10 instrument. Gas chromatographic analyses were carried out with a Carlo Erba Fractovap 4130 chromatograph. Flash chromatography was performed on silica gel (Merck, 230–240 mesh; 0.040–0.063 mm).

Reagents and solvents

All reactions were performed under argon in Schlenk tubes using vacuum line techniques. THF was dried and deoxygenated; it was carefully distilled under nitrogen from sodium benzophenone ketyl. Samarium powder (40 mesh) was purchased from Labelcomat. Samarium diiodide and sodium cyclopentadienide were prepared by the previously described procedure [7].

Samarium dicyclopentadienide

Samarium diiodide (0.1 M in THF, 60 ml, 6 mmol) was slowly added to 0.4 M solution of sodium cyclopentadienide in THF (30 ml, 12 mmol). A dark purple precipitate formed immediately, and was decanted within 1 h. The precipitate was washed twice with THF to remove sodium iodide. SmCp_2 can be stored for a few days in a Schlenk tube in THF without decomposition.

Standard procedure for Barbier reactions

A mixture of the carbonyl compound (2 mmol) and alkyl iodide (2 mmol) in 20 ml THF was added to Cp_2Sm (6 mmol) in 90 ml THF. The purple precipitate disappeared and the solution turned dark green then yellow within a few minutes. After 1 h the solution was treated with 0.1 N HCl. Extraction with ether, followed by washing of the extract with water and brine then evaporation left the crude product, which was purified by flash chromatography on a silica column. It was analyzed by GLC, GC/MS, and ^1H NMR spectroscopy.

Dihydro-5-butyl-5-methyl-2-(3H)-furanone (3). NMR (CDCl_3): 0.93 (t, $J = 6$ Hz, 3H), 1.2–1.4 (m, 4H), 1.39 (s, 3H), 1.9–2.2 (m, 2H), 2.55–2.65 (m, 2H). Mass

spectrum (70 eV), m/e (relative intensity): 141 (5.6 $M^+ - CH_3$); 99 (100, $M^+ - C_4H_9$).

Dihydro-5-methyl-5-(methylethyl)-2-(3H)-furanone (4). NMR ($CDCl_3$): 0.93 (2d, $J = 6$ Hz), 6H), 1.25 (m, 1H), 1.32 (s, 3H), 1.85–2 (m, 2H), 2.5–2.7 (m, 2H). Mass spectrum (70 eV), m/e relative intensity: 127 (5.1, $M^+ - CH_3$); 99 (100, $M^+ - C_3H_7$).

3-Methyl-1-decen-4-ol (7a). NMR ($CDCl_3$): 0.90 (t, 3H), 1.03 (d, 3H), 1.3 (m, 10H), 2.15–2.35 (m, 1H), 3.35–5.35 (m, 1H), 5–5.15 (m, 1H), 5.17 (s, 1H), 6.7–6.9 (m, 1H). Mass spectrum (70 eV), m/e relative intensity: 170 (0.5, M^+); 115 (8.8).

2-Undecen-5-ol (7b). NMR ($CDCl_3$): 0.91 (t, 3H), 1.3 (m, 10H), 1.68 (dd, 3H), 2.04 (m, 1H), 2.22 (m, 1H), 3.5–3.65 (m, 1H), 5.35–5.7 (m, 2H). Mass spectrum (70 eV), m/e relative intensity: 170 (1.2, M^+); 115 (6.8).

Ethyl-3-hydroxy nonanoate (9). NMR ($CDCl_3$): 0.90 (m, 3H), 1.27 (m, 13H), 2.5 (d, 2H), 2.7 (s, 1H), 4–4.4 (m, 3H). Mass spectrum (70 eV) m/e relative intensity: 201 (0.4, $M^+ - H$); 185 (0.8, $M^+ - OH$); 184 (0.8, $M^+ - H_2O$); 139 (66); 138 (5.6); 117 (100).

Ethyl-3-hydroxy-4,4-dimethylpentanoate (10). NMR ($CDCl_3$): 0.9 (s, 9H), 1.28 (t, 3H), 2.5 (d, 2H), 3.0 (d, 1H), 3.1–3.3 (m, 1H), 4.2 (q, 2H). Mass spectrum (70 eV) m/e relative intensity: 141 (0.9, $M^+ - H_2O - CH_3$); 129 (3.7 $M^+ - C_2H_5O$); 117 (72.1, $M^+ - C_4H_9$); 89 (37.5); 71 (100).

Acknowledgement

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