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Note

Catalytic auto-condensation of 2,4-pentanedione promoted by Sm(III) acetylacetonate: the X-ray structure of a novel complex $[Sm(CH_3COO)_3(H_2O)_2](H_2O)_2$

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Abstract

An efficient one-pot catalytic method to obtain 4,6-dimethyl-2-hydroxyacetophenone (A) is reported, the reaction proceeds via the intermolecular auto-condensation of 2,4-pentanedione using samarium(III) acetylacetonate ($Sm(AcAc)_3$) as promoter. A novel complex [$Sm(CH_3COO)_3(H_2O)_2$]($H_2O)_2$ (I) was isolated from the reaction media. The structure of I was determined by X-ray crystallography showing that the central atom is ennea-coordinated (monocapped square-antiprism geometry). This complex I also shows activity in the named autocondensation reaction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic auto-condensation; Sm(III) acetylacetonate; Metallic acetylacetonates; Homogeneous catalysis

1. Introduction

There are some reports on the use of Sm^{3+} compounds as catalytic promotors with applications in organic chemistry, e.g. condensation between 2,4-pentanedione with benzaldehyde assisted by Sm^{3+} , to produce α,β -unsatured carbonylic compounds [1] and the addition of α -haloketones to carbonylic compounds [2], the product obtained in both the cases was probably based on the Lewis acidity of Sm^{3+} species. A similar type of product viz. 4,6-dimethyl-2-hydroxyacetophenone, an interesting molecule with analgesic and antiinflammatory properties [3], is normally produced by phenol acylation [4] or through a Fries rearrangement [5] or even synthesized by autocondensation of pentanedione on refluxing for a long period in presence of a basic media with low yields and complicated work-up [6].

Here we wish to report the catalytic autocondensation of 2,4-pentanedione in the presence of $Sm(AcAc)_3$ to give 4,6-dimethyl-2-hydroxyacetophenone (**A**) in one step as the regiospecific product, we also observed the presence of some by-products (**B**, **C** and **D**) (Fig. 1). In addition, from the reaction mixture a novel complex $[Sm(CH_3COO)_3(H_2O)_2](H_2O)_2$ was obtained. Some other metal acetylacetonates (M(AcAc)_x) were also tested for the same reaction.

2. Experimental

2.1. Synthesis

Acetylacetonates of Co^{3+} , Fe^{3+} , La^{3+} and Co^{2+} were purchased from Aldrich Chemicals Company Inc. Acetylacetonates of Mn^{3+} , Ni^{1+} and Sm^{3+} were ob

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tained from Strem Chemical and 2,4-pentanedione was procured from Eastman Organic Chemical. All reactives were used without further purification.

2.2. Procedure

A mixture of pentanedione (116.85 mM) and $Sm(AcAc)_3$ (1.34 mM) were refluxed for 24 h. After this period, the solution was cooled to room temperature (r.t.), affording a solid product which was identified as the Sm complex (I) in 85.82% yield (m.p. > 270°C). The filtrate was analyzed on a Hewlett–Packard 5895 B, GC–MS equipment with a 25 m × 0.3 mm glass column packed with 5% phenyl silicone in order to characterize the other reaction products and quantified by GC in a Hewlett–Packard 5890 analyzer with a 30 m × 0.53 mm × 2.65 µm glass column packed with HP-1 crosslinked methyl silicone. The filtrate was concentrated and then treated with ethanol–water (1:2), affording a light-yellow crystalline compound, which



Fig. 1. By-products of the autocondensation of 2,4-pentanedione in the presence of $Sm(AcAc)_3$.



Fig. 2. ORTEP drawing of the complex [Sm(CH₃COO)₃(H₂O)₂](H₂O)₂.

Table 1

Crystal data and measurements conditions for complex $[Sm(CH_3COO)_3(H_2O)_2](H_2O)_2$

Crystal size (mm)	0.20 imes 0.10 imes 0.08
Formula	$C_{6}H_{17}O_{10}Sm$
Formula weight	399.55
Crystal system	Triclinic
Space group	$P\overline{1}$
Unit cell dimensions	
a (Å)	8.985(5)
$b(\dot{A})$	9.365(5)
$c(\dot{A})$	10.563
α (°)	91.630(5)
β(°)	113.960(5)
γ (°)	118.330(5)
$V(\dot{A}^3)$	687.4(6)
Z	2
$D_{\rm calc}$ (g cm ⁻³)	1.930
λ (Mo K α) (Å)	0.71069
μ (Mo K α) (mm ⁻¹)	4.307
Temperature (K)	293(2)
F(000)	390
Scan type	ω –2 $ heta$
Reflections collected	2558
Independent reflections	2390 $(R_{int} = 0.0364)$
Absorption correction	semi-empirical
Solution	SIR-92
Refinement method	full-matrix least-squares
Goodness-of-fit	1.005
R	0.0365
$R_{\rm w}$	0.0706
System used	SHELXL-97 (Sheldrick, 1997)
2	

was characterized by ¹H and ¹³C NMR as 4,6-dimethyl-2-hydroxyacetophenone (A), was isolated as the regiospecific product 75.65%.

A similar procedure was carried out with other metal acetylacetonates when used as promotors.

2.3. X-ray structure determination

Fig. 2 shows an ORTEP drawing of Sm complex I. X-ray crystallographic data were obtained on a Siemens P4/PC diffractometer using Mo K α radiation at r.t. Crystallographic data are given in Table 1. Selected bond distances and angles are presented in Table 2. The structure was solved by direct methods (SIR-92) [7] and refined by full-matrix least-squares on F^2 using SHELXTL-97 [8].

3. Results and discussion

The main product (A) can be formed by initial aldolic process (condensation–dehydration) followed by intermolecular ring closure after eliminating the second molecule of water, finally this ring is aromatized by tautomeric equilibria.

Table 2

Selected bond lengths (Å) and bond and torsion angles (°) for complex $[Sm(CH_3COO)_3(H_2O)_2](H_2O)_2$

Sm(1)–O(8)	2.398(4)	Sm(1)–C(1)	2.948(6)
Sm(1)–O(7)	2.417(4)	O(1)–C(1)	1.270(7)
Sm(1)–O(1) # 1	2.430(4)	$O(1)-Sm(1) \neq 1$	2.443(4)
Sm(1)–O(4)	2.462(4)	O(2) - C(1)	1.261(8)
Sm(1)–O(5)	2.477(4)	O(3) - C(3)	1.250(8)
Sm(1) - O(2)	2.495(5)	O(4) - C(3)	1.277(8)
Sm(1) - O(6)	2.497(5)	O(5) - C(5)	1.275(8)
Sm(1) = O(3)	2.501(5)	O(6) - C(5)	1 261(8)
Sm(1) = O(1)	2.586(8)	C(1)-C(2)	1 484(9)
Sm(1) - C(3)	2 864(6)	C(3) - C(4)	1 506(9)
Sm(1) - C(5)	2.869(6)	C(5) - C(6)	1.500(9)
	2.009(0)		02.02(17)
O(8) - Sm(1) - O(7)	/5.1/(1/)	O(8) - Sm(1) - O(1) # 1	83.82(17)
O(7)-Sm(1)-O(1) # 1	77.81(15)	O(8) - Sm(1) - O(4)	98.75(18)
O(7) - Sm(1) - O(4)	131.57(16)	O(1) # 1-Sm(1)-O(4)	150.34(16)
O(8) - Sm(1) - O(5)	125.34(17)	O(7) - Sm(1) - O(5)	144.24(15)
O(1) # 1-Sm(1)-O(5)	76.26(15)	O(4) - Sm(1) - O(5)	78.36(16)
O(8)-Sm(1)-O(2)	148.42(19)	O(7) - Sm(1) - O(2)	84.12(18)
O(1) # 1-Sm(1)-O(2)	115.12(14)	O(4) - Sm(1) - O(2)	77.37(18)
O(5)-Sm(1)-O(2)	85.04(17)	O(8) - Sm(1) - O(6)	74.24(17)
O(7)-Sm(1)-O(6)	143.08(17)	O(1) # 1-Sm(1)-O(6)	78.82(16)
O(4)–Sm(1)–O(6)	73.59(17)	O(5)–Sm(1)–O(6)	52.31(15)
O(2)-Sm(1)-O(6)	131.96(17)	O(8)–Sm(1)–O(3)	77.84(19)
O(7)–Sm(1)–O(3)	79.98(15)	O(1) # 1-Sm(1)-O(3)	154.15(15)
O(4)-Sm(1)-O(3)	52.21(15)	O(5)-Sm(1)-O(3)	129.39(15)
O(2)-Sm(1)-O(3)	75.23(17)	O(6)-Sm(1)-O(3)	112.82(17)
O(8)-Sm(1)-O(1)	139.25(15)	O(7)-Sm(1)-O(1)	73.55(15)
O(1) # 1-Sm(1)-O(1)	64.58(15)	O(4) - Sm(1) - O(1)	121.56(16)
O(5)-Sm(1)-O(1)	73.27(14)	O(2)-Sm(1)-O(1)	50.54(14)
O(6)-Sm(1)-O(1)	120.16(15)	O(3) - Sm(1) - O(1)	120.83(15)
O(8) - Sm(1) - C(3)	88.54(18)	O(7)-Sm(1)-C(3)	105.45(17)
O(1) # 1-Sm(1)-C(3)	170.66(15)	O(4) - Sm(1) - C(3)	26.40(17)
O(5)-Sm(1)-C(3)	104.11(16)	O(2)-Sm(1)-C(3)	74.12(16)
O(6) - Sm(1) - C(3)	93.95(18)	O(3)-Sm(1)-C(3)	25.82(17)
O(1)-Sm(1)-C(3)	124.64(15)	O(8)-Sm(1)-C(5)	99.60(18)
O(7)-Sm(1)-C(5)	153.30(17)	O(1) # 1-Sm(1)-C(5)	75.59(16)
O(4)-Sm(1)-C(5)	74.85(17)	O(5)-Sm(1)-C(5)	26.30(17)
O(2)-Sm(1)-C(5)	109.27(18)	O(6)-Sm(1)-C(5)	26.02(17)
O(3)-Sm(1)-C(5)	125.15(16)	O(1)-Sm(1)-C(5)	96.77(16)
C(3)-Sm(1)-C(5)	100.51(18)	O(8)-Sm(1)-C(1)	153.28(16)
O(7) - Sm(1) - C(1)	78.11(17)	O(1) # 1-Sm(1)-C(1)	90.06(14)
O(4) - Sm(1) - C(1)	99 34(18)	O(5) - Sm(1) - C(1)	77 73(15)
O(2) = Sm(1) = C(1)	25.07(16)	O(6) - Sm(1) - C(1)	130.03(16)
O(3) - Sm(1) - C(1)	98 16(17)	O(1) - Sm(1) - C(1)	25 47(15)
C(3)-Sm(1)-C(1)	99 17(17)	C(5)-Sm(1)-C(1)	$104\ 02(17)$
C(1)=O(1)=Sm(1) # 1	151 2(4)	C(1)=O(1)=Sm(1)	93 4(4)
O(4)-C(3)-Sm(1) = 1	59 0(3)	C(4)-C(3)-Sm(1)	177 3(5)
O(6) - C(5) - O(5)	119 7(6)	O(6) - C(5) - C(6)	121.8(6)
O(5) - C(5) - C(6)	118 6(6)	O(6) - C(5) - Sm(1)	60 3(3)
O(5) - C(5) - Sm(1)	50 4(3)	C(6) - C(5) - Sm(1)	177 7(5)
S(3)-C(3)-SIII(1)	J9.4(J)	$C(0) - C(0) - \operatorname{Sin}(1)$	1///(3)

The ring closure may ocurr at two different positions leading to two possible isomers, **A** and 2,6-dimethyl-4hydroxyacetophenone (**A**') (Fig. 3), however, the reaction is regiospecific and only gives **A**. The ring closure between C_1-C_6 may be favored because of the stabilization of the Sm³⁺ ion through the coordination with the acetylacetonate C₃-alkylated (in a six-membered arrangement), which is not possible in the other case if the ring closure occurs at C_7-C_2 . Additionally, a significant steric effect may also be involved in this unfavored pathway. Fig. 4 shows the (%) conversion versus time function. It was observed that the main product obtained was compound **A** and only a small amount of the by-products were detected in the reaction media. When complex **I** was used as a promotor in the same reaction we found an induction time in the reaction (Fig. 4), which may be due to the decomposition of the dimeric moiety in monomeric species containing acetylacetonate ligands in order to catalyse the transformation. In the absence of the Sm³⁺ species in the reaction media, no autocondensed product was obtained, sug-



Fig. 3. Sm^{3+} assisted pathway for C_1C_6 selective ring closure in autocondensation of 2,4-pentanedione.



Fig. 4. Catalytic autocondensation of pentanedione by $Sm(AcAc)_3$ (**■**) and complex **I** (**●**). In both (A) Main product and (B) + (C) + (D) byproducts. Condition 2,4-pentanedione (11.85 mM), promotor $Sm(AcAc)_3$ (1.34 mM), complex (**I**) (0.67 mM).

264 Table 3

4,6-Dimethyl-2-hydroxyacetophenone formation by catalytic autocondensation of 2,4-pentanedione mediated by $M(AcAc)_x^{a}$

Run	Catalyst	Total conversion (%)	Main product (%) (A)
1	$Co(AcAc)_2$	0.73	0.39
2	$Ni(AcAc)_2$	1.96	1.96
3	$Co(AcAc)_3$	1.39	1.39
4	Fe(AcAc) ₃	2.37	2.06
5	$Mn(AcAc)_3$	8.78	8.19
6	$La(AcAc)_3$	52.76	48.52
7	$Sm(AcAc)_3$	58.50	53.81
8	Sm(AcAc) ₃ ^b	91.22	75.65

 $^{\rm a}$ 116.85 mmol of 2,4-pentanedione and 1.34 mmol of catalyst, 24 h. $^{\rm b}$ $t=40\,$ h.

gesting that the substrate needs the presence of a Lewis acid to promote the reaction. Some other metal acetylacetonates were also tested in the process without exhibiting activity (Table 3), only samarium and lantane acetylacetonates gave good results.

The structure of the aquo carboxylate Sm³⁺ complex obtained from pentanedione and Sm(AcAc)₃ was determined by single-crystal data and revealed the follow composition, $[Sm(CH_3COO)_3(H_2O)_2](H_2O)_2$. The new complex formed in neutral conditions and appears as a dimer showing an Z,E-conformation with each Sm atom coordinated to three acetate ligand, two of these acetate anions act as bidentate ligand forming a fourmembered chelate ring and the third acetate anion acts as a tridentate ligand forming a bridge with a second Sm atom. In addition to each samarium atom there are two water molecules. The dimeric complex has crystallographic inversion symmetry. Both the Sm atoms are coordinated to nine oxygen atoms having monocapped square antiprism geometry with a oxygen atom of a bidentate acetate ligand at the cap position as shown in Fig. 2. The crystal structure of this complex shows the presence of acetate anion in the molecule, which was produced by the retrocondensation of pentanedione promoted by Sm^{3+} according to the following reaction:

$$CH_{3}COCH_{2}COCH_{3} + H_{2}O \rightleftharpoons CH_{3}COCH_{3}$$
$$+ CH_{3}COOH$$
(1)

The average M–O bond length around the Sm atom is 2.473(4) Å (2.398–2.586 Å). The bond length Sm(1)– O(1), 2.586(8) Å, is longer than Sm(1)–O(2), 2.495(5) Å, or Sm(1)–O(1)a, 2.430(4) Å, and the bond angles C(1)-O(2)-Sm(1), 98.0(3)°, C(1)-O(1)-Sm(1), 93.4(4)°, C(1)-O(1)-Sm(1)a, 151.2(4)°, are in the respective standard ranges of the *Z*,*E*-type acetate ligand. In crystal packing we observe the presence of intermolecular hydrogen bonds between the two dimeric units.

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