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## Chemoselective Reduction of Some Condensates derived from Chromone-3-carbaldehyde using Sm and Zn

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Abstract: Condensates 4-6 undergo reductive dimerization with Sm in THF containing aqueous NH<sub>4</sub>Cl to produce 7–9, whereas with Zn under similar reaction condition 3-5 produce 10-12.

**Keywords:** 1-Benzopyran; 3-formylchromone; reductive dimerisation; samarium reduction; zinc reduction

#### **INTRODUCTION**

Reductive dimerization of  $\alpha$ , $\beta$ -unsaturated carbonyl compound is a very important methodology in organic chemistry. Although SmI<sub>2</sub> has been used widely for this purpose,<sup>[1a]</sup> metallic samarium<sup>[1b]</sup> and zinc are also in use. High moisture and air sensitivity, difficulties in handling, and high cost restrict the use of SmI<sub>2</sub> in many cases. Sm- or Zn-induced reductive dimerization and cyclization of alkylidene malononitrile or cyanoacetate to aminocyclopentenes,<sup>[2]</sup> reductive dimerization and cyclization of  $\alpha$ , $\beta$ unsaturated carbonyl compounds by Sm/HgCl<sub>2</sub><sup>[3]</sup> or Zn/THF/H<sub>2</sub>O<sup>[4]</sup> to cyclopentanols, reductive dimerization of cinnamates by Sm/Al/ MeOH,<sup>[1b]</sup> pinacolization,<sup>[5]</sup> and allylation<sup>[6]</sup> using Sm metal have been reported. It has also been reported that the condensates derived from PhCHO and acetylacetone or ethyl acetoacetate or diethyl malonate failed to react with Sm powder,<sup>[2a]</sup> and a similar condensate from PhCHO

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and methyl  $\alpha$ -benzenesulphonylacetate undergoes desulfonylation when treated with Sm/HOAc in tetrahydrofuran (THF).<sup>[7]</sup>  $\alpha,\beta:\gamma,\delta$ -Unsaturated dienamide undergoes partial reduction to  $\beta,\gamma$ -unsaturated amide by Zn-HOAc.<sup>[8]</sup> So, it is of interest to study how the condensates **3–6** containing a chromone moiety as well as an  $\alpha,\beta:\gamma,\delta$ -unsaturated carbonyl or ester moiety will behave toward Sm or Zn metal. We have reported sodium naphthalenide–induced reductive coupling of chromone-3-carbaldehyde  $\mathbf{1}^{[9]}$  and methyl chromone-3-carboxylate **2**,<sup>[10]</sup> and Zn-induced chemoselective reductions of the condensate **6** in different media.<sup>[11]</sup> We report herein the differential behavior of Sm and Zn on the condensates **3–6**.

#### **RESULTS AND CONDITIONS**

On stirring, a mixture of the condensate 4 or 5 or 6 (1 mmol) and Sm powder (4 mmol) in THF (10 mL) containing saturated aqueous  $NH_4Cl$  solution (0.5 mL) at room temperature for several hours (Table 1)

Entry	Compound	Metal	Reaction medium <sup>a</sup>	Time (h)	Product	Yield (%)	Mp (°C)	
1	<b>4</b> a	Sm	А	15	7a	55	128-130	
2	<b>4</b> a	Zn	А	12	11a <sup>b</sup>	46	98-100	
3	4b	Sm	А	16	7b	60	106-108	
4	4b	Zn	А	12	11b <sup>b</sup>	40	88–90	
5	<b>4</b> c	Sm	А	15	7c	60	161-162	
6	<b>4</b> c	Zn	А	10	11c	45	98-100	
7	<b>3</b> a	Zn	А	25	10a	30	68-70	
8	3a	Sm	А	30		No reaction	L	
9	<b>3a</b>	Zn	В	10	10a	70	70	
10	5a	Zn	А	15	12a <sup>b</sup>	40	116	
11	5a	Sm	А	15	<b>8</b> a	60	98	
12	5b	Sm	А	25	8b	65	128-130	
13	6a	Sm	А	10	9a	65	177	
14	6b	Sm	А	10	9b	50	204	
15	6c	Sm	А	9	9c	55	163-164	
16	<b>3a</b>	Sm	В	18		No reaction		
17	<b>4</b> a	Sm	В	15		No reaction		
18	5a	Sm	В	10		No reaction		
19	6b	Sm	В	30		No reaction	L	

Table 1. Role of metal and reaction medium in the reduction of the condensates 3-6

<sup>*a*</sup>Reaction medium A: THF/saturated aqueous  $NH_4Cl$  solution. Reaction medium B: HOAc.

<sup>b</sup>Compounds have same mp and mmp as authentic samples.<sup>[11]</sup>



Scheme 1. Chemoselective reduction of 3-6.

produces dimers 7 or 8 or 9, respectively, in moderate yields. Under similar reaction conditions but using Zn powder (4 mmol) in place of Sm powder, compounds 3 or 4 or 5 undergo reduction of the exocyclic double bond to produce 10 or 11 or 12, respectively (Scheme 1). Although the condensates 4–6 derived from 1 and acetylacetone or ethyl benzoylacetate or ethyl cyanoacetate undergo Sm-induced dimerization, relatively less reactive condensate 3 arising from 1 and diethyl malonate gives back the starting material (80%) under similar reaction condition (entry 8, Table 1). Reduction of exocyclic double bond of 3 by Zn has been accomplished with greater efficiency by using HOAc in place of THF– aq NH<sub>4</sub>Cl as reaction medium (entries 7 and 9). Similar reactions of 4 and 5 with Zn in HOAc has been reported earlier.<sup>[11]</sup> Surprisingly, Sm fails to react with 3–6 when the reaction was carried out in HOAc (entries 16–19).

Reductive dimerization of the ester 2 with sodium naphthalenide<sup>[10]</sup> produces the 2,2'-coupled product without opening of the pyran ring, but Sm-mediated dimerization products 7–9 are formed by coupling through 2, 2'-position of the chromone ring followed by opening of the pyran ring and leads to the formation of a conjugated tetraene. To the best of our knowledge, it is the first example of Sm-induced reductive dimerization to produce a highly substituted conjugated tetraene. However, a monoterpenoid moiety, 1,10-diphenyl-3,8-dimethyldeca-3,7-diene-1,10-dione, has been synthesized by treating isoprene with benzoyl chloride in the presence of Sm in DMF at room temperature.<sup>[12]</sup>

It has also been observed that similar condensates derived from aliphatic aldehydes and active methylene compounds fail to dimerize by Sm-NH<sub>4</sub>Cl/THF-H<sub>2</sub>O for lack of radical stabilization.<sup>[2a]</sup> In the present work, pyran ring oxygen stabilizes the radical at the 2-position of the pyran ring and helps the reaction to proceed. It should be mentioned here that like sodium naphthalenide,<sup>[10]</sup> neither Zn nor Sm is capable of performing a dechlorination reaction under this reaction condition from the substrates **4c** and **6c** bearing chlorine on the phenyl rings of the chromone moieties.

In conclusion, we have reported Sm- and Zn-induced two chemoselective reductions of  $\alpha,\beta:\gamma,\delta$ -unsaturated carbonyl or ester moieties where the double bond at the  $\gamma,\delta$ -position is a part of the chromone ring. Sm-induced reductive dimerization of **4–6** constitutes a method for the synthesis of densely substituted conjugated tetraene.

#### **EXPERIMENTAL**

Melting points are determined in an open capillary and are uncorrected. IR spectra were recorded on a Beckman IR 20A in KBr discs, <sup>1</sup>H NMR in CDCl<sub>3</sub> with TMS as an internal standard on a Bruker 300-MHz spectrometer, mass spectra on Qtof Micro YA 263 instrument, and elemental analysis on a Perkin-Elmer 240C element analyser. Light petroleum refers to the fraction with distillation range 60–80°C. Sm powder was obtained from CDH Chemicals, India.

# General Procedure for the Treatment of Condensates 4–6 with Sm Powder

Sm powder (600 mg, 4 mmol) was added to a THF solution (10 mL) of condensate 4 or 5 or 6 (1 mmol). After stirring for 5 min, saturated aqueous solution of NH<sub>4</sub>Cl (0.5 mL) was added. The reaction mixture became reddish immediately and was stirred at room temperature for several hours as mentioned in Table 1. After completion of the reaction (monitored by thin-layer chromatography, TLC), the reaction mixture was filtered, and the residue was washed with THF. Solvent was removed from the filtrate under reduced pressure; crushed ice (20 g) was added to the concentrate. In the case of substrate 4 or 5, a solid mass separated, which was then filtered, dried in air, and recrystallized from benzene-petroleum ether to produce 3,10diacetyl-5,8-di(2-hydroxy-5-substituted/unsubstitutedbenzoyl)dodeca-3,5, 7,9-tetraene-2,11-dione 7 or diethyl 2,9-dibenzoyl-4,7-di(2-hydroxy-5-substituted/unsubstitutedbenzoyl)deca-2,4,6,8-tetraenedioate 8, respectively. With condensate 6 as substrate, an oily mass was obtained after addition of ice water into the concentrate. The oily mass was extracted with CHCl<sub>3</sub>  $(2 \times 10 \text{ mL})$ , washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and chromatographed over silica gel (100–200). Diethyl 2,9-dicarbamoyl-4,7-di(2-hydroxy-5-substituted/unsubstitutedbenzoyl)deca-2,4,6,8-tetraenedioate **9** was isolated using benzene as eluent. Yields and mp of **7–9** are mentioned in Table 1.

#### Data

Compound **7a**. Yellow crystalline compound. Found: C, 70.10; H, 5.00%.  $C_{30}H_{26}O_8$  requires C, 70.03; H, 5.09%,  $\nu_{max}$  (KBr) 3430, 2925, 1686, 1633, 1587, 1205 cm<sup>-1</sup>;  $\delta_H$  11.77 (2H, s, exchangeable, 2 × OH), 8.88 (2H, d, J = 1.3 Hz, 2 × vinylic H), 8.29 (2H, d, J = 1.3 Hz, 2 × vinylic H), 7.60–7.53 [4H, m, 2 × (4-H and 6-H)], 7.11 (2H, dd, J = 8.4, 1.0 Hz, 2 × 3-H), 6.96–6.91(2H, m, 2 × 5-H), 2.86 (6H, s, 2 × COCH<sub>3</sub>) and 2.66 (6H, s, 2 × COCH<sub>3</sub>); MS (positive ion electrospray): m/z 514(M<sup>+</sup>), 513(M<sup>+</sup>-H).

Compound **7b**. Yellow crystalline compound. Found: C, 70.70; H, 5.61%.  $C_{32}H_{30}O_8$  requires C, 70.84; H, 5.57%.  $\nu_{max}$  (KBr) 3427, 3076, 2928, 1685, 1629, 1593, 1209 cm<sup>-1</sup>;  $\delta_H$  11.59 (2H, s, exchangeable, 2 × OH), 8.87 (2H, d, J = 1.5 Hz, 2 × vinylic H), 8.29 (2H, d, J = 1.5 Hz, 2 × vinylic H), 7.39 (2H, dd, J = 8.4, 1.2 Hz, 2 × 4-H), 7.31 (2H, d, J = 1.2 Hz, 2 × 6-H), 7.02 (2H, d, J = 8.4 Hz, 2 × 3-H), 2.87 (6H, s, 2 × COCH<sub>3</sub>), 2.66 (6H, s, 2 × COCH<sub>3</sub>) and 2.28 (6H, s, 2 × ArCH<sub>3</sub>); MS (positive ion electrospray): m/z 271(M<sup>+</sup>/2), 270(M<sup>+</sup>/2-H).

Compound 7c. Yellow crystalline compound. Found: C, 61.65; H, 4.20%.  $C_{30}H_{24}Cl_2O_8$  requires C, 61.76; H, 4.14%.  $\nu_{max}$  (KBr) 3430, 3072, 2930, 1680, 1635, 1590, 1215 cm<sup>-1</sup>;  $\delta_H$  11.65 (2H, s, exchangeable, 2 × OH), 8.88 (2H, d, J = 1.2 Hz, 2 × vinylic H), 8.28 (2H, d, J = 1.2 Hz, 2 × vinylic H), 7.52–7.50 [4H, m, 2 × (4-H and 6-H)], 7.07 (2H, d, J = 8.4 Hz, 2 × 3-H), 2.87 (6H, s, 2 × COCH<sub>3</sub>) and 2.67 (6H, s, 2 × COCH<sub>3</sub>).

Compound **8a**. Yellow crystalline compound. Found: C, 72.30; H, 4.85%.  $C_{42}H_{34}O_{10}$  requires C, 72.20; H, 4.90%.  $\nu_{max}$  (KBr) 3450, 3055, 2980, 1713, 1626, 1587, 1211 cm<sup>-1</sup>;  $\delta_{H}$  11.81 (2H, s, exchangeable, 2 × OH), 9.04 (2H, d, J = 2.0 Hz, 2 × vinylic H), 8.41 (2H, d, J = 2.0 Hz, Hz, 2 × vinylic H), 7.62–7.56 (8H, m, ArH), 7.49–7.47 (6H, m, ArH), 7.13 (2H, dd, J = 8.1, 1.0 Hz, 2 × 3-H), 6.98–6.93(2H, m, 2 × 5-H), 4.21 (4H, q, J = 7.0 Hz, 2 × OCH<sub>2</sub>) and 1.09 (6H, t, J = 7.0 Hz, 2 × CH<sub>3</sub>); MS (positive ion electrospray): m/z 349 (M<sup>+</sup>/2).

Compound **8b**. Yellow crystalline compound. Found: C, 72.65; H, 5.30%. C<sub>44</sub>H<sub>38</sub>O<sub>10</sub> requires C, 72.72; H, 5.27%.  $\nu_{max}$  (KBr) 3440, 3050, 2975, 1710, 1625, 1580, 1215 cm<sup>-1</sup>;  $\delta_{\rm H}$  11.64 (2H, s, exchangeable, 2 × OH), 9.03 (2H, d, J = 1.1 Hz, 2 × vinylic H), 8.42 (2H, d, J = 1.1 Hz, Hz, 2 × vinylic H), 7.69–7.59 (4H, m, ArH), 7.53–7.45 (6H, m, ArH),

7.43–7.34 (4H, m, ArH), 7.03 (2H, d, J = 8.2 Hz,  $2 \times 3$ -H), 4.21 (4H, q, J = 7.0 Hz,  $2 \times \text{OCH}_2$ ), 2.29 (6H, s,  $2 \times \text{ArCH}_3$ ) and 1.10 (6H, t, J = 7.0 Hz,  $2 \times \text{CH}_3$ ); MS (positive ion electrospray): m/z 725 (M<sup>+</sup>-H), 363 (M<sup>+</sup>/2), 362(M<sup>+</sup>/2-H).

Compound **9a**. Yellow crystalline compound. Found: C, 62.32; H, 4.92; N 4.90%.  $C_{30}H_{28}N_2O_{10}$  requires C, 62.50; H, 4.89; N, 4.86%.  $\nu_{max}$  (KBr) 3430, 3140, 1695, 1630, 1618, 1596, 1235 cm<sup>-1</sup>;  $\delta_{\rm H}$  11.75 (2H, s, exchangeable, 2 × OH), 8.61 (2H, d, J = 1.8 Hz, 2 × vinylic H), 8.59 (2H, d, J = 1.8 Hz, 2 × vinylic H), 8.03 (2H, brs, exchangeable, 2 × NH), 7. 58 (2H, dd, J = 7.5, 1.8 Hz, 2 × 6-H), 7.52–7.50 (2H, m, 2 × 4-H), 7.05 (2H, dd, J = 8.2, 1.8 Hz, 2 × 3-H), 6.92–6.90 (2H, m, 2 × 5-H), 5.81 (2H, brs, exchangeable, 2 × NH), 4.40 (4H, q, J = 7.0 Hz, 2 × OCH<sub>2</sub>) and 1.38 (6H, t, J = 7.0 Hz, 2 × CH<sub>3</sub>); MS (positive ion electrospray): m/z 288(M<sup>+</sup>/2), 287(M<sup>+</sup>/2-H).

Compound **9b**. Yellow crystalline compound. Found: C, 63.72; H, 5.39; N 4.69%.  $C_{32}H_{32}N_2O_{10}$  requires C, 63.57; H, 5.33; N, 4.63%.  $\nu_{max}$  (KBr) 3438, 3140, 1700, 1630, 1620, 1590, 1212 cm<sup>-1</sup>;  $\delta_H$  11.60 (2H, s, exchangeable, 2 × OH), 8.62–8.61 (4H, m, 4 × vinylic H), 8.05 (2H, brs, exchangeable, 2 × NH), 7.38 (2H, d, J = 2.0 Hz, 2 × 6-H), 7.34 (2H, dd, J = 8.4, 2.0 Hz, 2 × 4-H), 6.99 (2H, d, J = 8.4 Hz, 2 × 3-H), 5.81 (2H, brs, exchangeable, 2 × NH), 4.38 (4H, q, J = 7.1 Hz, 2 × OCH<sub>2</sub>), 2.29 (6H, s, 2 × ArCH<sub>3</sub>) and 1.39 (6H, t, J = 7.1 Hz, 2 × CH<sub>3</sub>).

Compound **9c**. Yellow crystalline compound. Found: C, 55.90; H, 4.10; N 4.26%.  $C_{30}H_{26}N_2Cl_2O_{10}$  requires C, 55.73; H, 4.06; N, 4.34%.  $\nu_{max}$  (KBr) 3435, 3135, 1690, 1625, 1620, 1590, 1230 cm<sup>-1</sup>;  $\delta_H$  11.65 (2H, s, exchangeable, 2 × OH), 8.63 (2H, d, J = 2.1 Hz, 2 × vinylic H), 8.59 (2H, d, J = 2.1 Hz, 2 × vinylic H), 8.13 (2H, brs, exchangeable, 2 × NH), 7.57 (2H, d, J = 2.5 Hz, 2 × 6-H), 7.46 (2H, dd, J = 8.9, 2.5 Hz, 2 × 4-H), 7.04 (2H, d, J = 8.9 Hz, 2 × 3-H), 5.87 (2H, brs, exchangeable, 2 × NH), 4.39 (4H, q, J = 7.1 Hz, 2 × OCH<sub>2</sub>), and 1.40 (6H, t, J = 7.1 Hz, 2 × CH<sub>3</sub>).

#### General Procedure for the Reaction of Zn with Condensates 3-5

To a solution of condensate 3 or 4 or 5 (1 mmol) in THF (10 mL), Zn powder (250 mg, ~4 mmol) and saturated aqueous solution of NH<sub>4</sub>Cl (0.5 mL) were added, and the reaction mixture was stirred at room temperature for 6 h. The resulting mixture was filtered, residue was washed with THF. All the washings and filtrate were mixed, and solvent was removed under reduced pressure. Crushed ice (10 g) was added, and a semisolid mass was obtained. It was extracted with CHCl<sub>3</sub>, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and chromatographed over silica gel (100–200)

#### Sm and Zn-induced Chemoselective Reduction

to afford compounds 10, 11, and 12 from the reaction of 3, 4, and 5 respectively. Yields and mp of 10, 11, and 12 are mentioned in Table 1.

#### Data

**Diethyl 2-(chromone-3-yl)methylpropanedioate** (10a). White crystalline compound. Found: C, 64.06; H, 5.75%.  $C_{17}H_{18}O_6$  requires C, 64.14; H, 5.70%.  $\nu_{max}$  (KBr) 2984, 2941, 1743, 1728, 1643, 1464, 1257 cm<sup>-1</sup>;  $\delta_{H}$  8.22 (1H, dd, J = 7.9, 1.0 Hz, 5-H), 7.89 (1H, s, 2-H), 7.66 (1H, m, 7-H), 7.44–7.38 (2H, m, 6-H and 8-H), 4.18 (2H, q, J = 7.0 Hz, OCH<sub>2</sub>), 4.17 (2H, q, J = 7.0 Hz, OCH<sub>2</sub>), 3.97 (1H, t, J = 7.6 Hz, CH), 3.02 (2H, d, J = 7.6 Hz, CH<sub>2</sub>) and 1.22 (6H, t, J = 7.0 Hz, 2 × CH<sub>3</sub>).

**3-(6-Chlorochromone-3-yl)methylpentane-2,4-dione (11c).** White crystalline compound. Found: C, 61.50; H, 4.45%.  $C_{15}H_{13}ClO_4$  requires C, 61.55; H, 4.48%.  $\nu_{max}$  (KBr) 3395, 3070, 2930, 1715, 1698, 1635 cm<sup>-1</sup>;  $\delta_{\rm H}$  16.86 (1H, s, exchangeable, enolic OH), 8.21 (1H, d, J = 2.3 Hz, 5-H, enol), 8.15 (1H, d, J = 2.5 Hz, 5-H, keto), 7.94 (1H, s, 2-H, keto), 7. 64–7.59 (2H, m, 7-H, keto + enol), 7.55 (1H, t, J = 1.1 Hz, 2-H, enol), 7.42 (1H, d, J = 8.8 Hz, 8-H, keto), 7.41 (1H, d, J = 9.0 Hz, 8-H, enol), 4.27 (1H, t, J = 6.7 Hz, methine H, keto), 3.51 (2H, d, J = 1.1 Hz, CH<sub>2</sub>, enol), 2.98 (2H, d, J = 6.7 Hz, CH<sub>2</sub>, keto), 2.26 (6H, s, 2 × COCH<sub>3</sub>, keto) and 2.12 (6H, s, 2 × COCH<sub>3</sub>, enol). (keto-enol 5:3).

Compounds **11a**, **11b**, and **12a** are identical in all respect to authentic samples.<sup>[11]</sup>

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