An environmentally benign catalytic oxidation of cholesteryl acetate with molecular oxygen by using *N*-hydroxyphthalimide

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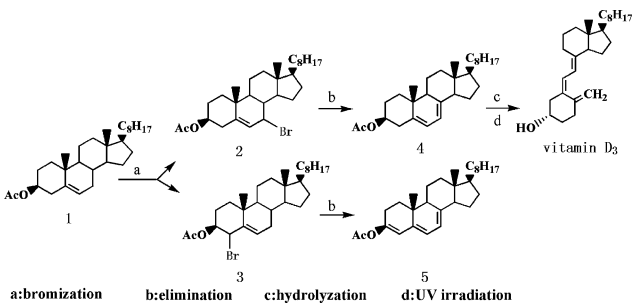
A green and effective method is reported for the oxidation of cholesteryl acetate to 7-keto-cholesteryl acetate with O_2 in the presence of catalytic amounts of *N*-hydroxyphthalimide (NHPI) under mild conditions. It was found that $Co(OAc)_2$ could cooperate with $Mn(OAc)_2$ to enhance the catalytic ability of NHPI resulting in better yields. This economical and environmentally-friendly method provides a potentially new way for the synthesis of the intermediate product of vitamin D_3 in industry, which eliminates the use of large amounts of bromine in present route and overcomes the drawbacks of the known oxidation methods.

Introduction

The allylic oxidation of cholesteryl acetate to 7-keto-cholesteryl acetate is quite important due to its various applications in the synthesis of pharmaceuticals and fine chemicals.[1–3] One of the most important applications is the synthesis of vitamin D_3, which is of great interest because vitamin D_3 plays an essential role in the maintenance of organic systems.[4] Nowadays, some of the vitamin D_3 used worldwide is synthesized using the strategy depicted in Scheme 1,[5,6] in which, the use of large amounts of bromine is unavoidable, thereby resulting in bromine-related corrosion and environmental hazards. In addition, undesirable side products (such as compounds **3** and **5**, Scheme 1) cannot be avoided in this process. Therefore, the production of vitamin D_3 by a halogen-free method is vital for the industry from an environmental point of view and has become a focus of scholastic interests. An innovative strategy (Scheme 2) for the synthesis of 7-dehydrocholesteryl acetate (**4**), which is the intermediate product of vitamin D_3, has been developed.[7,8] This method can overcome the above mentioned drawbacks, in which, the oxidation of cholesteryl acetate to 7-keto-cholesteryl acetate (**6**), is the crucial step, while the following synthesis



Scheme 1 Traditional synthesis of vitamin D_3.

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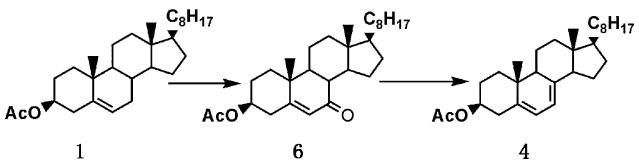


Scheme 2 Novel synthesis of 7-dehydrocholesteryl acetate (**4**).

of **4**, hydrolyzation and UV irradiation are relatively mature processes.[6,8]

Various methods have been developed for the oxidation of cholesteryl acetate, which is the initial material of vitamin D_3. They can be divided into two groups: (i) reactions wherein metal derivatives are used. The well-known classical method is chromium(VI) oxide mediated oxidation using CrO_3[9] or PDC[10] and $Cr(CO)_6$[11] in acetic acid. A great excess of the reagents and a large volume of the solvent are required in most of these procedures, as is complicated work-up of the environmentally hazardous chromium residues, therefore making these methods inconvenient. (ii) Reactions wherein peroxides are used. For example, *t*-butyl hydroperoxide (TBHP) with different catalysts, such as sodium chlorite,[12,13] cuprous iodide[14] and manganese(III) acetate.[15] These routes are obviously more environmentally benign than those discussed above,[9–11] however, TBHP is too expensive for large-scale industrial application.

The methods mentioned above turned out to be unsuitable for the oxidation from both an economic and environmental point of view. Molecular oxygen is the ideal oxidant for large scale processing, however, it cannot be directly utilized to oxidate substrates. As a result, many high efficient catalysts have been developed to catalyze molecular oxygen for the oxidations.[16–18] Recently, a new organic catalyst, *N*-hydroxyphthalimide (NHPI), has been introduced as an effective catalyst for C–H bond activation by hydrogen abstraction,[19–24] which is a cheap, non-toxic compound easily prepared by the reaction of phthalic anhydride with hydroxylamine.[25] Due to its idiosyncratic behaviour, which is very different from that of any system proposed previously, and

to its general efficiency, NHPI has attracted increasing attention in the past decade, from both in academia and the industries.

Herein, we present an improvement of the NHPI system, which opens up a new and efficient access to 7-keto-cholesteryl acetate. Molecular oxygen is introduced as oxidant, and only catalytic amounts of NHPI is used with a better yield, which has never been achieved before. This environmentally reliable and practical method holds promising application potential for chemical industries, particularly in the synthesis of vitamin D_3, for this easy method can substitute the bromination in the traditional route (Scheme 1).

Experimental

Chemicals

All the chemicals were of AR grade. They were commercially purchased and used without further treatment.

Synthesis of 7-keto-cholesteryl acetate

In a typical experiment, a solution of 0.163 g (1 mmol) of NHPI in 80 mL of acetone was poured in a three-necked 100 mL round-bottom flask, equipped with a magnetic stirrer and a reflux condenser. 4.28 g (10 mmol) of cholesteryl acetate and co-catalyst used as described in the manuscript were added into the flask. A stream of dioxygen was conducted into the reaction solution while stirring at room temperature for 8 h. The reaction mixture was rotary-evaporated (bath temperature 40–50 °C). In order to separate the catalysts from the reaction mixture, the residue was treated with 30 mL of hexane and heated to 40 °C. After the reaction mixture was cooled to room temperature, the resulting finely crystalline precipitate NHPI was filtered out, and dried (0.149 g, 92%). The filtrate was rotary-evaporated at 60 °C to constant mass. Then, the oily residue was treated with 5 mL of acetic anhydride in an alkalescent system and stood at room temperature overnight. As a dehydrating agent, acetic anhydride can convert the primary and secondary hydroperoxides into corresponding compounds (ketones), resulting in higher yields. The mixture was then concentrated on a rotary evaporator. The residue was treated with 10 mL of methanol and the resulting suspension was cooled in an ice-bath for 1 h and then suction filtered. Recrystallization of 7-keto-cholesteryl acetate from the residue gave 3.78 g (86%) of the product (158–159 °C). [In order to check whether the product can be used to synthesize vitamin D_3, we synthesized vitamin D_3 according to known methods:[6,8] 0.442 g (1 mmol) 7-keto-cholesteryl acetate and 0.186 g (1 mmol) 4-methylbenzenesulfonhydrazide were added into the flask. After stirring at room temperature for 20 h, the reaction mixture was rotary-evaporated. The residue was treated with 25 mL dimethyl sulfoxide and stoichiometric amounts of sodium hydride while stirring at room for 6 h. Ethyl acetate was used for extraction in neutral solutions. 7-Dehydrocholesteryl acetate was obtained with a yield of 60% after rotary evaporation. A 3% solution of 7-dehydrocholesterol in a methanol mixture was irradiated with a XeBr lamp at 284 nm in a falling-film reactor. The selectivity of vitamin D_3 in the reaction mixture is 90%, with a conversion of 50%.]

Table 1 Oxidation of cholesteryl acetate with different amounts of NHPI[a]

Entry	NHPI/mmol%	t/h	Conversion[b] (%)	Isolated yield (%)
1	10	14	20	11
2	50	13	96	60
3	100	9	96	69[c]
4	200	3.5	96	53

[a] Reaction conditions: cholesteryl acetate (4.28 g, 10 mmol), acetone (80 mL), BPO (0.016 g, 0.5 mmol) room temperature, O_2 1 atm. [b] Conversion rates of cholesteryl acetate were calculated using HPLC analysis, and were unchanged after the reaction hours showed above. [c] Isolated yield in ref. 26 and 27 was 73.8% under the same conditions.

Results and discussion

Early research indicated that NHPI can efficiently oxidate substrates with molecular oxygen by adding a small amount of radical starters, such as dibenzoyl peroxide (BPO).[26,27] In a first set of experiments, the influence of the amount of NHPI on the reaction was investigated (Table 1). After an initial sharp increase in the conversion rate and percentage yield, an optimal yield was obtained in the presence of about 100 mol% NHPI, followed by a slow decrease as the amount of NHPI was further increased. To ensure that the reaction gives the desired yield, stoichiometric amounts of NHPI must be used (entry 3). Therefore, the oxidation route lacked competitive ability compared with the present bromination route from an economical point of view, because of the large amounts of NHPI as well as a yield of 69%. Lesser amounts of catalysts and higher yields of products were always the ultimate goal in industrial application. However, as shown in Table 1, when the amount of NHPI was dropped to 10 mol%, both the reaction rate and selectivity significantly decreased.

It is crucial for the oxidation of cholesterol using a catalytic amount NHPI in high yield. The previously known processes showed that the reactivity of NHPI can be enhanced by adding different co-catalysts.[28–30] We found that the yields were improved to some extent no matter what kind of metal salt was used (Table 2). However, the yields were lower when trivalent metal salts ($Co(III)(acac)_3$, $Fe(III)(acac)_3$, $Fe(III)(acac)_3Cl_3$, entries 1–3) were used as co-catalysts. Bivalent metal salts ($Co(II)(acac)_2$,

Table 2 Oxidation of cholesteryl acetate with NHPI by different co-catalysts[a]

Entry	Co-catalysts[b]/mmol	t/h	Conversion[c] (%)	Isolated yield (%)
1	$Co(acac)_3$/0.1	10	99	41
2	$Fe(acac)_3$/0.1	6	91	28
3	$Fe(acac)_3Cl_3$/0.1	8	91	39
4	$Co(acac)_2$/0.1	7	91	50
5	$Mn(OAc)_2$/0.1	12	91	66
6	$Co(OAc)_2$/0.1	8	96	59

[a] Reaction conditions: cholesteryl acetate (4.28 g, 10 mmol), NHPI (0.163 g, 1 mmol), acetone (80 mL), room temperature, O_2 1 atm. [b] $Co(acac)_3$: cobalt(III) acetylacetonate, $Fe(acac)_3$: ferric acetylacetonate, $Fe(acac)_3$-Cl_3: 3-chlorine-acetylacetonate ferric, $Co(acac)_2$: cobalt(II) acetylacetonate, $Mn(OAc)_2$: manganese acetate, $Co(OAc)_2$: cobalt(II) acetate. [c] Conversion rates of cholesteryl acetate were calculated using HPLC analysis, and were unchanged after the reaction hours showed above.

Table 3 Oxidation of cholesteryl acetate with different ratios of $Co(OAc)_2$ to $Mn(OAc)_2$ as co-catalyst[a]

Entry	Catalyst-system: NHPI/mmol	Catalyst-system: $Co(OAc)_2$ and $Mn(OAc)_2$/mmol	t/h	Conversion[b] (%)	Isolated yield (%)
1	1	0.07/0.03	8	95	64
2	1	0.05/0.05	8	98	86
3	—	0.05/0.05	14	24	14
4	1	0.05/0.05[c]	8	97	76
5	1	0.03/0.07	8	94	69

[a] Reaction conditions: cholesteryl acetate (4.28 g, 10 mmol), acetone (80 mL), room temperature, O_2 1 atm. [b] Conversion rates of cholesteryl acetate were calculated using HPLC analysis. [c] $Co(acac)_2$ and $Mn(OAc)_2$/mmol: 0.05/0.05.

$Mn(II)(OAc)_2$, $Co(II)(OAc)_2$, entries 4–6) gave better yields under the same conditions. NHPI acts as a precursor of the phthalimido-*N*-oxyl (PINO) radical, generated with the assistance of metal salts.[31] The transition metal ions worked by forming oxo-transition metal intermediates, thereby relaying oxygen atom from the oxidant to the cholesteryl acetate. This requires the transition metal ions to be capable of readily losing one electron (*e.g.*, Co(II)–Co(III) and Mn(II)–Mn(III)), which may explain why bivalent metal salts are more effective than trivalent ones that are far more reluctant to lose electrons.[32]

We noticed that reaction rates were higher with Co(II) salts as co-catalyst (entries 4 and 6), and the yields were higher with Mn(II) salts (entry 5). This inspired us that a combination of both a Co(II) salt and Mn(II) salt should give better yields and faster reaction rates. To test this hypothesis, we ran the reaction with different ratios of $Co(OAc)_2$ to $Mn(OAc)_2$ as co-catalyst. With the total amount of co-catalyst kept invariant, the isolated yield with the addition of Mn(II) salts reached a maximum when the ratio of $Co(OAc)_2$ to $Mn(OAc)_2$ was 1 : 1, then dropped as the amount of Mn(II) salts further increased (Table 3). The best result (86%, entry 2) was obtained using a combination of NHPI and mixtures of $Co(OAc)_2$ and $Mn(OAc)_2$ at room temperature in acetone, with shorter reaction time but higher yield compared with previous methods.[9–15,26,27] A combination of $Co(acac)_2$ and $Mn(OAc)_2$ under the same conditions gave a yield of 76% (entry 4). Blank experiments were carried out to reveal that a mixture of $Co(OAc)_2$ and $Mn(OAc)_2$ or NHPI as the sole catalyst led only to extremely low yields of products after 14 h (entry 3, Table 3; entry 1, Table 1).

Further research was performed to oxidize cholesteryl acetate with this catalyst system under different reaction conditions. Reaction temperatures from 50 °C to 20 °C (Table 4, entries 1–5) were investigated. The reaction time and the isolated yields increased as the temperature dropped, the isolated yield reached a maximum at 25 °C and then decreased. Higher temperature enhanced substrate solubility and shortened the reaction time. However, they gave lower yields. At 50 °C, the solvent was volatilized and the formation of by-products made likely, resulting in low yields (entry 1). At 20 °C, the solubility of cholesteryl acetate was poor, and the yield went down to 51% (entry 5). The optimal reaction temperature was experimentally determined to be 25 °C. Different solvents were also used under the same mild conditions (entries 6 and 7), which revealed

Table 4 Oxidation of cholesteryl acetate with the optimized catalyst-system in different conditions[a]

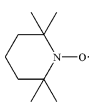
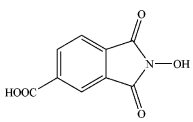
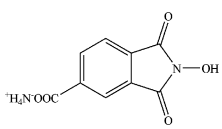
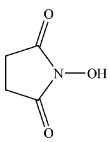
Entry	Solvent	T/°C	Conversion[b] (%)	Isolated yield (%)
1	Acetone	50	97	63
2	Acetone	40	91	78
3	Acetone	30	96	83
4	Acetone	25	98	86
5	Acetone	20	93	51
6	THF	25	90	50
7	1,4-Dioxane	25	96	78

[a] Reaction conditions: cholesteryl acetate (4.28 g, 10 mmol), NHPI (0.163 g, 1 mmol), $Co(OAc)_2$ (0.0125 g, 0.05 mmol), $Mn(OAc)_2$ (0.0123 g, 0.05 mmol), acetone (80 mL), room temperature, O_2 1 atm, 8 h. [b] Conversion rates of cholesteryl acetate were calculated using HPLC analysis.

acetone to be the best solvent. These results indicated that the reaction gave the best yields at ambient temperature and atmospheric pressure of oxygen, both favourable for industrial application.

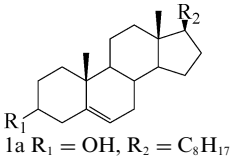
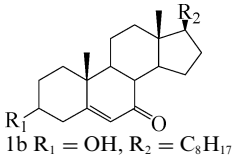
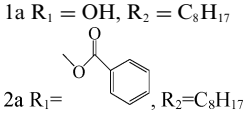
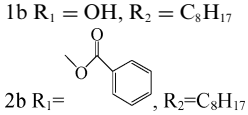
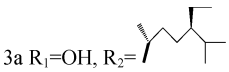
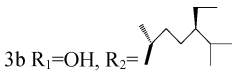
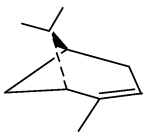
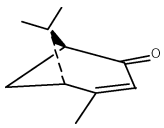
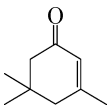
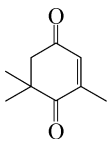
Based on the above-mentioned results, NHPI was revealed to be a key catalyst. To find the best catalytic system, allylic oxidation of cholesteryl acetate as a model substrate, was studied under the same conditions in the presence of several other nitroxy radicals (Table 5). When the persistent tetramethylpiperidine-*N*-oxyl (TEMPO) radical, being a widely used catalyst for the oxidation of alcohols,[31] was used it in our allylic oxidation, only 9% cholesteryl acetate was converted (entry 1). The NHPI derivatives such as *N*-hydroxy trimellitic imide and its ammonium salt were also investigated, which

Table 5 Oxidation of cholesteryl acetate with different nitroxy radicals[a]

Entry	Nitroxy radicals	t/h	Conversion[b] (%)	Isolated yield (%)
1		12	9	—
2[c]		12	23	22
3[c]		12	20	13
4		12	61	47

[a] Reaction conditions: cholesteryl acetate (4.28 g, 10 mmol), nitroxy radicals (1 mmol), $Co(OAc)_2$ (0.0125 g, 0.05 mmol), $Mn(OAc)_2$ (0.0123 g, 0.05 mmol), acetone (80 mL), room temperature, O_2 1 atm. [b] Conversion rates of cholesteryl acetate were calculated using HPLC analysis. [c] Solvent: acetone 50 mL, acetonitrile 30 mL.

Table 6 Oxidation of different hydrocarbons with the optimized catalyst system[a]

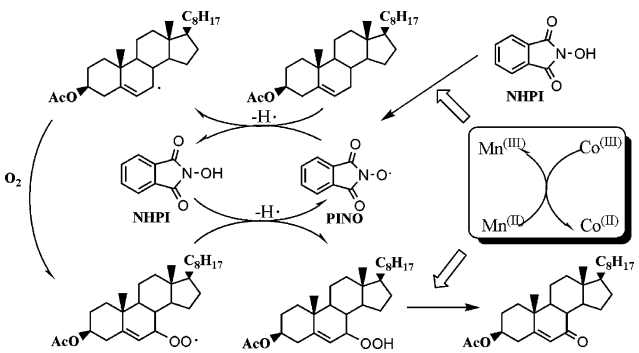
Entry	Substrate	Product	Conversion[b] (%)	Isolated yield (%)
1	 1a $R_1 = OH$, $R_2 = C_8H_{17}$	 1b $R_1 = OH$, $R_2 = C_8H_{17}$	95	78
2[c]	 2a R_1=, R_2=C_8H_{17}	 2b R_1=, R_2=C_8H_{17}	93	66.
3[c]	 3a R_1=OH, R_2=	 3b R_1=OH, R_2=	91	68
4[d]			61	14[e]
5[d]			5	4

[a] Reaction conditions: substrate (10 mmol), NHPI (0.163 g, 1 mmol), $Co(OAc)_2$ (0.0125 g, 0.05 mmol), $Mn(OAc)_2$ (0.0123 g, 0.05 mmol), acetone (80 mL), room temperature, O_2 1 atm, 8 h. [b] Conversion rates of cholesteryl acetate were calculated using HPLC analysis. [c] Solvent: 1,4-dioxane 80 mL. [d] Conversion rate and yield were calculated by TLC. [e] Yield was increased to 34% after 15 h.

resulted in relatively low conversions and yields (entries 2 and 3). A better result was achieved when the reaction was carried out in the presence of *N*-hydroxysuccinimide (entry 4), however, the yield was much lower than the best result obtained above (Table 3, entry 2). These results indicated that using NHPI as the key catalyst proved efficient both with respect to the final yields and the reaction times of the referred reaction.

The optimized amounts of NHPI and co-catalysts were further employed to catalyze oxygenations of various hydrocarbons. Relatively good results were achieved using steroid analog as substrates (Table 6, entries 1–3), which have similar structure with cholesterly acetate. Cholesterol was oxygenated with high conversions and converted selectively to 7-keto-cholesterol with 78% isolated yield (entry 1). The oxidation of cholesteryl benzoate and β-sitosterol were also proceeded smoothly in 1,4-dioxane because of their poor solubility in acetone (entries 2 and 3). Essentially, the reaction of the steroid analogs belonged to allylic oxidation. Two simple model substrates with the possibility to be oxidized at the allylic site were investigated (entries 4 and 5). The 61% of α-pinene was converted in 8 h, giving a yield of 14% (entry 4). The yield was increased to 34% after 15 h. However, it was found that α-isophorone cannot be oxidized to ketoisophorone easily (entry 5). This may explained by the conjugative effect of double bond and carbonyl, which made α-isophorone difficult to be oxidized.

A plausible reaction mechanism for the allylic oxidation of cholesterol catalyzed by NHPI and transition metal salts is shown in Scheme 3. The *in situ* generation of PINO from NHPI through redox reaction of transition metal salts is a key step.[32] In the next step, a hydrogen atom is abstracted from the cholesterol to form an alkyl radical. The resultant alkyl radical is trapped by the peroxy radicals provided by dioxygen, and eventually converted into oxygenated products. The synergistic effects of $Co(OAc)_2$ and $Mn(OAc)_2$ also suggested the presence of a radical transformation step in the course of the oxidation.[20,21]



Scheme 3 A plausible mechanism for the allylic oxidation of cholesteryl acetate catalyzed by NHPI and transition metal salts.

Conclusion

In summary, we have developed an effective method to oxidate cholesteryl acetate to 7-keto-cholesteryl acetate by molecular oxygen under mild conditions. This economical and environmentally-friendly procedure led to good yields with a

small amount of catalyst, and could eliminate the use of a large amounts of bromine used in the present route of vitamin D_3 and overcome the drawbacks of the known oxidation methods.

Further research in cooperative catalysis with $Co(OAc)_2$ and $Mn(OAc)_2$ should lead to a universal method for the effective usage of NHPI. Our research in this field and in other aerobic oxidations for the vitamin industry are in progress.[33–36]

Acknowledgements

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