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A Short Review of Methods for the Allylic Oxidation of Δ^5 Steroidal Compounds to Enones

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Abstract

Introduction of α, β-unsaturated ketones to Δ^5 steroidal olefins changes the characteristics and biological function of those compounds. Several synthetic methods have been reported to accomplish carbonyl introduction to Δ^5 steroidal olefins. Herein, this short review will catalogue many of those oxidative methods, particularly those proceeding through a peroxide intermediate and/or use chromium complexes as reagents.

Keywords: Allylic oxidation; TBHP; Chromium; Steroids

Introduction

The oxidation of the B ring in steroidal compounds leads to products exhibiting numerous biological functionalities. Ring B oxidized sterols and steroids have shown anti-cancer activity [1-3]. 7-Ketodehydroepiandrosterone has been shown to improve the memory of mice [4] and 3-acetyl-7-oxo-DHEA increases the resting metabolism of persons on calorie restrictive diets [5]. 7-Ketopregnenolone's has shown anti-cortisone properties [6]. 7-Ketocholesterol has shown some regulatory function in the biosynthesis of cholesterol [7]. Furthermore, B ring oxidized steroidal compounds may be used as synthetic reagents to make other steroidal products, such as a steroidal pyrazoline [8].

Several Δ^5 allylic oxidation methods leading to enone formation have been reported and are catalogued in this review. The Δ^5 steroidal olefins are very common. Other steroidal olefins, with the exception of Δ^4 olefins perhaps, are much less common. As the precursor of steroids, cholesterol's Δ^5 moiety is retained until the steroids are enzymatically isomerized [9]. Thus, methods stated in this review have many potential steroidal substrates.

There are three allylic carbons (C4, C7 and C10) to the C5 double bond in a typical steroidal nucleus before isomerization to Δ^4. The C10 carbon is a stable quaternary carbon. Thus, allylic oxidation occurs only at C4 and C7, albeit not equally. The C4 carbon is located on the sterically hindered β side with its axial hydrogen extending also in the β direction. On the other hand, the C7 carbon is located on the exposed α side with its axial hydrogen extending further in the α direction [10]. There is also an energetic advantage for C7 oxidation. Resonance originating from C7 oxidation is more energetically favored than resonance originating from C4 oxidation due to delocalization to the tertiary C5 carbon rather than to the secondary C6 carbon. It was calculated that radical oxidation at C7 is favored by -4.65 kcal/mol over C4 on a two ring system containing the A and B ring moiety of cholesterol [11] (Figure 1). It should be noted as an exception that selenium complexes have been reported to oxidize C4 rather than C7 [12,13].

Steroidal compounds can be fairly resistant to deprotonation, especially within the B ring. Ring strain, that is incurred from the sp^3 to sp^2 hybridization change (bond angle distortion), is higher than that of non-fused ring systems due to "conformational transmission" [14]. Perhaps this explains why the oxidative methods surveyed in Tables 1-5 occur exclusively through a radical mechanism. With respect to the radical mechanism, it is important to note that tertiary carbons are present on steroidal compounds that can be radically oxidized leading to undesired side products, one in particular being C25 for steroids with side chains [15]. Furthermore, cleavage of the side chain can occur concurrent with allylic oxidation [16].

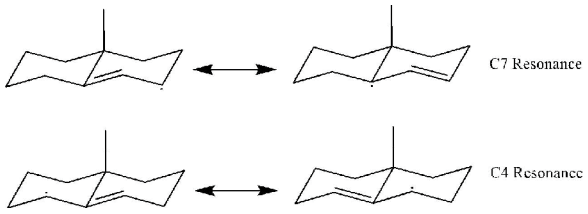

Figure 1: C4 and C7 resonance demonstrated by a two ring system with a similar moiety [11].

Protecting the C3 hydroxy group is commonly accomplish by esterification using acetic anhydride to make cholesteryl acetate. The authors of this review prefer esterification with benzoyl chloride since cholesteryl benzoate products can be more easily isolated with recrystallization in acetone and water than the steroidal acetates. This esterification is necessary because many oxidants and catalysts will convert the C3 hydroxyl group to a ketone [17].

Due to interest in "green" or environmentally benign chemistry, chemists have questioned the ethics of earlier catalysts. Environmental and health concerns have motivated the search for new oxidants and catalysts [18]. From chromium based catalysts, the next phase in steroidal allylic oxidation manifested through more environmentally friendly metallic catalysts that use TBHP as an oxygen donor. Meanwhile, several methods have been reported to give steroidal oxidation without any metal catalysts using as sodium chlorite and sodium hypochlorite [19,20]. Additionally, recoverable heterogeneous catalysts, clay

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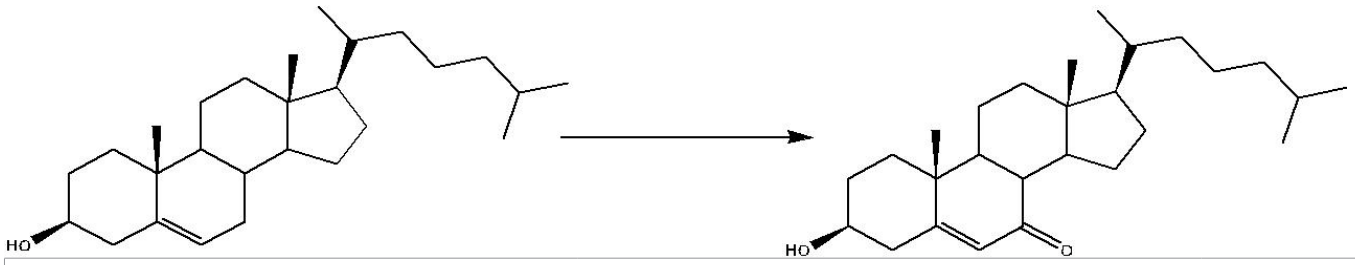
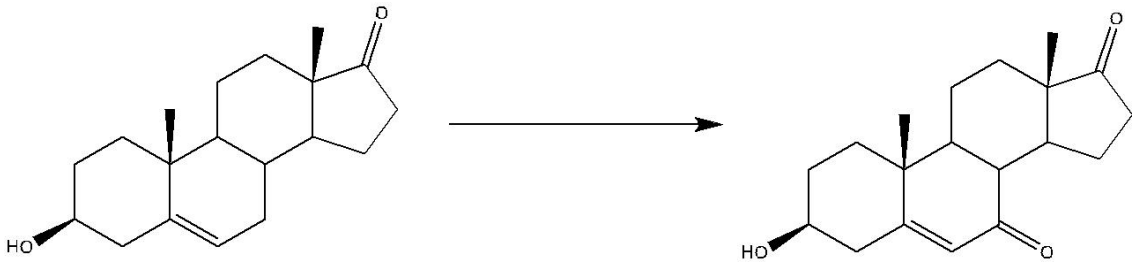


Substrate: Cholesterol				
Catalysts, Reagents, Solvents and Conditions	**TBHP used as Oxidant (Yes/No)**	**Date Reported**	**% Yield Reported**	**Reference #**
$Rh_2(cap)_4$, DCM (DCE), r.t, 15 h	Yes	2009	30	[26]
$Rh_2(cap)_4$, DCM (DCE), r.t, 20 h	Yes	2007	63	[27]
NaOCl, DCE, 4°C, 10 h	Yes	2004	68	[20]
CrO_3/NHPI-activated clay, DCM, r.t, 58 h	No	2009	52	[21]
2-quinoxalinol salen Cu(II) complex catalyst, Acetonitrile, 70°C, 12 h	Yes	2010	69	[11]
$RuCl_3$, Cyclohexane, r.t, 24 h	Yes	1996	51	[28]
$VOCl_3$, r.t, 5 days	Yes	2015	45	[29]

Table 1: Cholesterol to 7-ketocholesterol.



Substrate: DHEA				
Catalysts, Reagents, Solvents and Conditions	**TBHP used as Oxidant (Yes/No)**	**Date Reported**	**% Yield Reported**	**Reference #**
$Rh_2(cap)_4$, DCE, 40°C, 20 h	Yes	2007	74	[27]
NaOCl, Ethylacetate/Tert-butanol (8:2), 4°C, 10 h	Yes	2004	70	[20]
CrO_3/NHPI-activated clay, DCM, r.t, 58 h	No	2009	67	[21]
$BiCl_3$, Acetonitrile, 70°C, 28 h	Yes	2005	80	[30]
$BiCl_3$/K-10, Acetonitrile, 70°C, 11 h	Yes	2005	77	[30]
$NaClO_2$, Acetonitrile/Water (2:1), 50°C, 20 h	Yes	2007	65	[19]
$NaClO_2$/NHPI, Acetonitrile/Water (2:1), 50°C, 11 h	No	2007	50	[19]
$VOCl_3$, r.t, 5 days	Yes	2015	19	[29]

Table 2: DHEA to 7-keto DHEA.

supported and organometallic polymer catalysts, have been reported to yield allylic oxidation products of steroidal compounds [21–23].

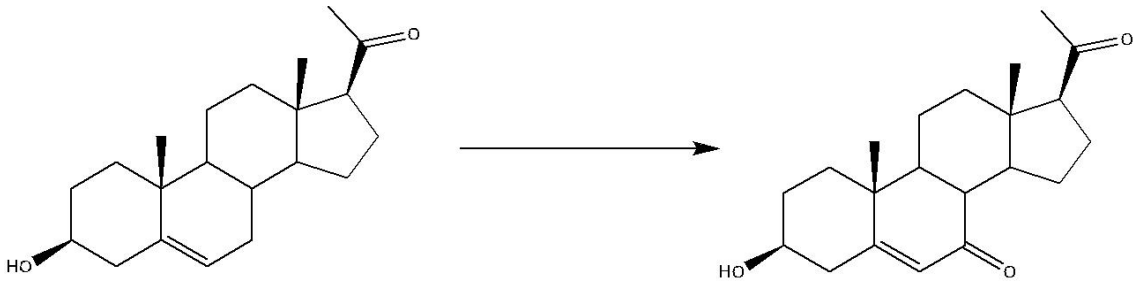
Reported Methods

The following Tables 1-5 are divided by substrates used in our allylic oxidation reaction with TBHP and vanadium complexes. Reagents, conditions, dates, and isolated yields reported for various steroidal allylic oxidation reactions are displayed. All reagents are listed, with TBHP given a special column (TBHP was mainly, if not exclusively used).

Caution must be taken when comparing the reported yields because there were various methods used to identify "isolated" yields (using HPLC instead of obtaining mass for example) [20], differing standards on purity of the isolated product (i.e., reporting an isolated yield that is 67% pure) [19], differing sampling sizes, and an overall lack of supporting information. Several reported steroidal allylic oxidation reactions have not been included in the tables due to low yields of 7-keto product, such as oxygen irradiation with and without photosensitizer [24] and Gif chemistry [25].

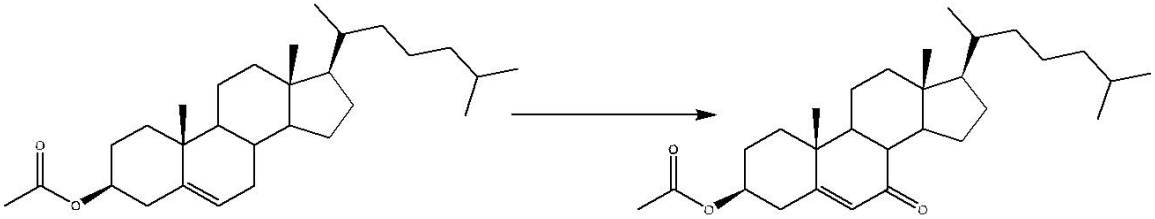
The importance of identifying TBHP usage in allylic oxidation reactions is that those reactions share a similar intermediate. It has been noted, "that different catalysts produce essentially the same mixture of products with the same relative yields suggests that the catalyst is not involved in product-forming steps" [26]. Indeed, tert-butoxide and tert-butyl peroxy radicals are formed through degradation of TBHP by catalysts. Those radicals then oxidize steroidal compounds [19,20,26-33,36].

All of the reactions in Table 1-5 can be funneled, generally speaking, into two mechanisms. The first mechanism, oxidation through formation of a C7 peroxide, is shared by auto-oxidation, TBHP-metal



Substrate: Pregnenolone				
Catalysts, Reagents, Solvents and Conditions	**TBHP used as Oxidant (Yes/No)**	**Date Reported**	**% Yield Reported**	**Reference #**
$Rh_2(cap)_4$, DCE, 40°C, 20 h	Yes	2007	40	[27]
CrO_3/NHPI-activated clay, DCM, r.t, 58 h	No	2009	54	[21]
2-Quinoxalinol salen Cu(II) complex catalyst, Acetonitrile, 0°C, 12 h	Yes	2010	53	[11]
$VOCl_3$, r.t., 5 days	Yes	2015	24	[29]

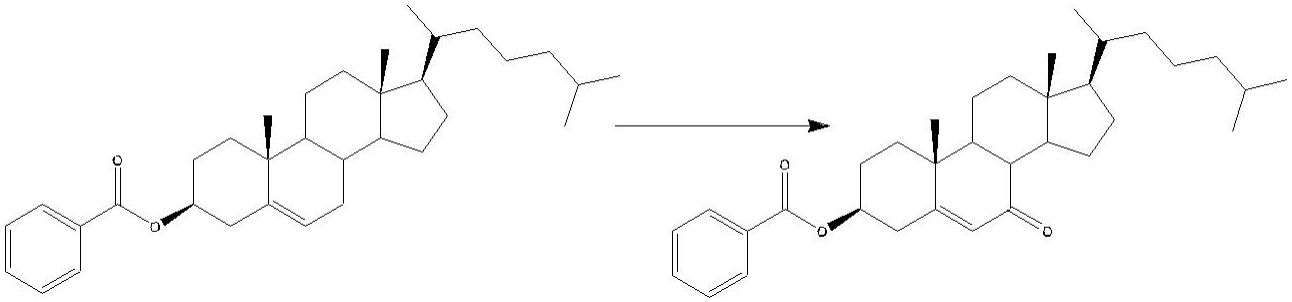
Table 3: Pregnenolone to 7-ketopregnenolone.



Substrate: Cholesteryl Acetate				
Catalysts, Reagents, Solvents and Conditions	**TBHP used as Oxidant (Yes/No)**	**Date Reported**	**% Yield Reported**	**Reference #**
$Co(OAc)_2/SiO_2$, Benzene, 50°C, 24 h, N_2	Yes	2001	70	[22]
ZrO_2/SiO_2/Cr(VI), Benzene, r.t, pH 3	Yes	1999	48	[31]
$RuCl_3$, Cyclohexane, r.t, 24 h	Yes	1996	51	[28]
$Rh_2(cap)_4$, DCE, 40°C, 20 h	Yes	2007	80	[27]
$TiO(acac)_2$, Benzene, 80°C, 24 h, Ar	Yes	1981	25	[32]
98 $VO(acac)_2$, Benzene, 80°C, 24 h, Ar	Yes	1981	26	[32]
$Cr(acac)_3$, Benzene, 80°C, 24 h, Ar	Yes	1981	52	[32]
$Mn(acac)_2$, Benzene, 80°C, 24 h, Ar	Yes	1981	11	[32]
$Mn(acac)_3$, Benzene, 80°C, 24 h, Ar	Yes	1981	10	[32]
$Fe(acac)_3$, Benzene, reflux, 24 h, Ar	Yes	1979	74	[32]
$Co(acac)_2$, Benzene, 80°C, 24 h, Ar	Yes	1981	12	[32]
$Co(acac)_3$, Benzene, 80°C, 24 h, Ar	Yes	1981	43	[32]
$Ni(acac)_2$, Benzene, 80°C, 24 h, Ar	Yes	1981	38	[32]
$Cu(acac)_2$, Benzene, 80°C, 24 h, Ar	Yes	1981	83	[32]
$Ce(acac)_2$, Benzene, 80°C, 24 h, Ar	Yes	1981	24	[32]
$Cu(Oac)_2/SiO_2$, Benzene, 70°C, 48 h, N_2	Yes	2002	72	[23]
CuI, Acetonitrile, reflux, 4 h	Yes	2003	79	[33]
CuI/TBAB, DCM, reflux, 4 h	Yes	2003	76	[33]
CrO_3/Py_2, Triflourotoluene, r.t, 31 h, N_2	Yes	2006	76	[34]
CrO_3/Py_2, DCM, r.t, 24 h, N_2	No	1969	74	[10]
PCC, DCM, 40°C, 66 h	Yes	2006	41	[34]
CrO_2, Acetonitrile/Benzene (9:1), reflux, 72 h, N_2	No	Note	48	
$Cr(CO)_6$, Acetonitrile, reflux, 15 h	Yes	1985	80	[35]
$Mn_3O(Oac)_9$, Ethyl Acetate, 40°C, 48 h, N_2	Yes	2006	87	[36]
NaOCl, DCE, 4°C, 10 h	No	2004	68	[20]
2-QuinoxalinolsalenCu(II) complex catalyst, Acetonitrile, 70°C, 12 h	Yes	2010	97	[11]
$BiCl_3$, Acetonitrile, 70°C, 22 h	Yes	2005	82	[30]

$NaClO_2$, Acetonitrile, 60°C, 80 h	Yes	2007	66	[19]
$NaClO_2$/NHPI, 1,4-dioxane/water (3:1), 50°C, 25 h	No	2007	60	[19]
$VOCl_3$, r.t, 5 days	Yes	2015	83	[29]

Table 4: Cholesteryl acetate to 7-ketocholesteryl acetate.



Substrate: Cholesteryl Benzoate'				
Catalysts, Reagents, Solvents and Conditions	**TBHP used as Oxidant (Yes/No)**	**Date Reported**	**% Yield Reported**	**Reference #**
PFC, Benzene, reflux, 48 h, N_2	No	1996	88	[37]
CrO_2, Acetonitrile/benzene (9:1), reflux, 72 h, N_2	No	Note	52	[35]
CrO_3/DMP, DCM, -10°C to -20°C, 4 h	No	1978	75	[38]
PCC, Benzene, refluxed, 24 h, N_2	No	1987	87	[39]
$VOCl_3$, r.t, 5 days	Yes	2015	98	[29]

Table 5: Cholestryl benzoate to 7-ketocholesteryl benzoate.

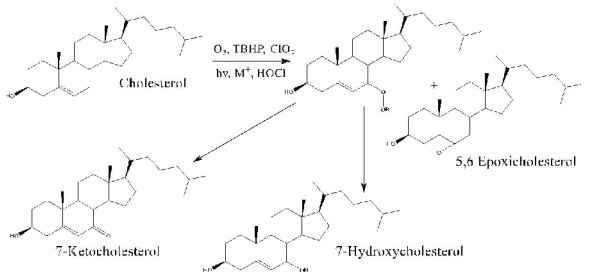


Figure 2: TBHP and singlet oxygen oxidation's shared mechanism. 5,6-epoxicholesterol may be a side product.

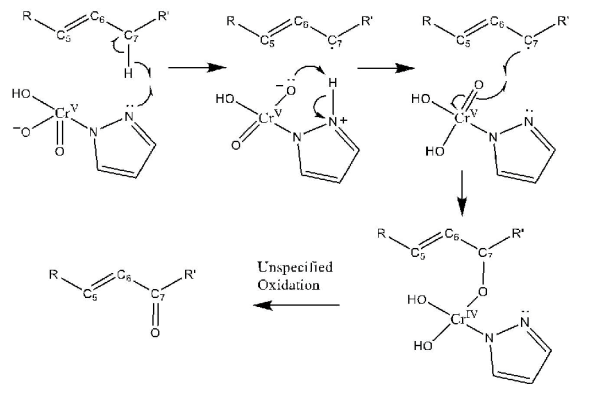


Figure 3: Suggested mechanism of allylic oxidation by chromium [38].

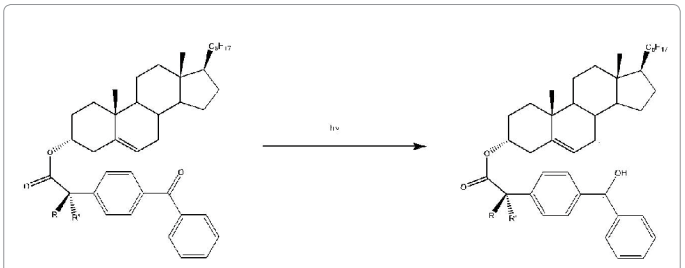


Figure 4: Hydrogen abstraction in benzophenoneaminocholestene [43].

oxidation, and hypochlorite oxidation. In auto-oxidation, a peroxide is formed via singlet oxygen (ene reaction) at the C5 carbon [24], which rearranges to the C7 position [40,41]. Likewise, TBHP degradation by metal leads to radicals that form a C7 peroxide. Bleach initiates radical formation from TBHP, similar to the metal catalysts [20]. When only sodium chlorite and NHPI are used, NHPI becomes phthalimide N-oxyl (PINO), a radical initiator of molecular oxygen [19]. Those radicals in addition to radicals formed from ClO_2 lead to a C7 peroxide. The C7 peroxide degrades to form a ketone or hydroxyl group [40-42] (Figure 2).

The second mechanism is that of oxidation via chromium reagent. During the first step of the suggested mechanism (Figure 3), there is complexation of chromium and a ligand containing a functional group, imine preferably, such as DMP or pyridine. After complexation, the ligand abstracts the C7 hydrogen leaving a resonating steroidal radical. An oxo group on the chromium complex will terminate the radical, reducing the chromium. Oxidation of the steroid then proceeds in an unspecified manner. It is important to note that the chromium complex may be monomeric [38].

Acetonitrile, benzene, pyridine, DCM, DCE, trifluorotoluene, 1,4-dioxane/water, and cyclohexane were used as solvents in Tables 1-5. Using laser flash photolysis and benzophenoneaminocholestene, it has been shown that the C7 hydrogens are abstracted at a much greater rate (more than double) in DCM than in acetonitrile, dioxane, and

methanol [43] (Figure 4). Thus, the least polar solvents appear to work best for allylic oxidation. This is, however, limited by the solubility of the steroidal substrate.

Conclusion

Converting Δ^5 steroidal compounds to their corresponding enones is an endeavor that has spanned several decades. The authors of this review suggest that all of the oxidative methods found within this review utilize one of two general mechanisms. One mechanism involves formation of a peroxide at the allylic position and the other achieves oxidation through reduction of a chromium complex. Both mechanisms occur via radical formation. Various solvents were used in the reported methods, but flash photolysis experiments from at least one article indicate that nonpolar solvents may be more affective.

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