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An efficient and convenient transformation of α-haloketones to α-hydroxyketones using cesium formate

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ABSTRACT

A new safe and convenient transformation has been developed. In the presence of cesium formate in dry MeOH solution, α-haloketones underwent direct conversion reaction to afford α-hydroxyketone in excellent yields. Furthermore, this methodology can be extended and applied in 2-chloro-*N*-(1,3-diphenyl-1*H*-pyrazol-5-yl)acetamide, 2-chloro-*N*-(2,6-dimethylphen-yl)acetamide, 1-(bromomethylsulfonyl)benzene, and *N*-(bromomethyl)phthalimide to give the corresponding products in moderate to excellent yields.

1. Introduction

α-Hydroxyketone moieties are structural features [1–7] and synthetic precursors [8–11] of various biological-active compounds and natural products. General synthetic methods for their preparation include the irradiation α-haloketones under microwave [12] or under a high-pressure mercury lamp condition [13], α-hydroxylation of an enolate with a molybdenum peroxide [14–17] or the other oxidizing agents [18], transformation of the enamine derivatives by molecular oxygen [19], metallic-catalyzed oxidative transformation of olefins [20–23] and hydroxylation of silyl enol ether with *m*-chloroperbenzoic acid [24,25] or with certain oxidizing agents [26,27]. Most of the synthetic methodology could not provide satisfactory reaction conditions due to the expensive and special instruments required or the expensive and dangerous heavy metal oxidizing agents needed. As a result, development of the direct and non-toxic methods is considered enthusiastically for the synthesis of α-hydroxyketones.

Cesium bases have demonstrated several merits in organic synthetic reactions [28–34], highlighted by comparative high solubilities [35], appropriate basicities and good stabilities [36–41]. In this work, we reported a safe and convenient method for the preparation of α-hydroxyketones from α-haloketones by using cesium formate (HCO_2Cs). Direct transformation of α-haloketones in the presence of cesium formate in dry MeOH afforded α-hydroxyketones in good to excellent yields.

2. Result and discussion

We chose the strictly geometric 21-bromo-3α-hydroxyl-3β-methoxymethyl-5α-pregnan-20-one (**1**) [42] as the model for the selection of best solvents for the transformation. Compound **1** was allowed to react with different equivalent of NaOH in different solvents, including THF, THF/water, DMF, EtOH, wet MeOH, and dry MeOH. We found the use of 3.0 equiv of NaOH in dry MeOH gave the corresponding products **1b** and **1c** in ~50% total yield as the best results (~50%, see Scheme 1). As a result, dry MeOH was chosen as the solvent for the transformation of α-haloketones in the following studies.

To investigate the effect of alkali-metal ions, we treated a dry MeOH solution of 21-bromo-3α-hydroxyl-3β-methoxymethyl-5α-pregnan-20-one (**1a**) in dry MeOH with 5.0 equivlents of the different bases including lithium, sodium [43], and potassium hydroxide, and sodium, potassium, and cesium formates at reflux. After normal workup and purification with column chromatography on silica gel, the desired α-hydroxyketones (**1b** and **1c**) were isolated as solids (see Scheme 1 and Table 1). Among the bases, we found that the use of alkali formate gave better results (80–87% yields) than the use alkali hydroxides (16–57% yields). The longer reaction time was also required for alkali hydroxides (>48 h). Of the alkali formates for the reaction, sodium [44–46], potassium [46], and

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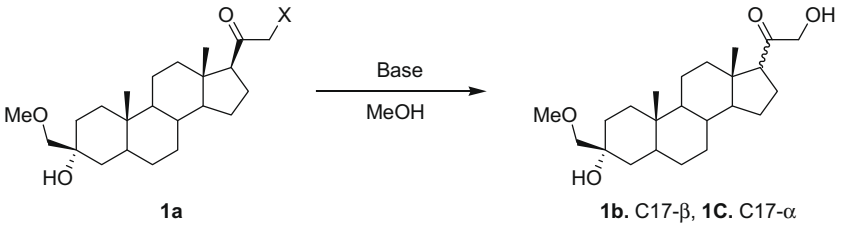


1a **1b.** C17-β, **1C.** C17-α

Scheme 1.

Table 1
Hydrolysis reaction of 21-bromo-3α-hydroxyl-3β-methoxymethyl-5α-pregnan-20-one (**1a**) with various bases.

Entry	Bases	Reaction time (h)	Yields (**1b** + **1c**, %)	Ratio of **1b/1c** (C17-β/C17-α)
1	LiOH	>48	17	–
2	NaOH	>48	51	–
3	KOH	>48	57	–
4	HCO_2Na	15	80	88/12[a]
5	HCO_2K	15	81	93/7[a]
6	HCO_2Cs	12	87	98/2[a]

[a] The area normalization was focused on **1b/1c** (C-17β/C-17α) ratio and detected by the column separation.

cesium formats [47] were most efficient bases to provide the hydrolysis products **1b** and **1c** in high yield (80–87%, see Table 1). The reactivity of hydroxyl and formate anion is reported to depend on the ability of alkali-metal to dissociate from hydroxyl ($^-$OH) and formate (HCO_2^-) counterions [48,49]. Our study showed the reactivity of hydrolysis were KOH > NaOH > LiOH and HCO_2Cs > HCO_2K > HCO_2Na. These results were consistent with the literature dissociation order of counterion [48,49].

For the regioseletivity of the alkali formats toward transformation, we detected the ratio of **1b/1c** (C-17β/C-17α) for the conversion reaction by the column separation. We found the lower C-17β/C17α ratio and yield were obtained by using HCO_2Na (see entry 4 in Table 1). When we used HCO_2K or HCO_2Cs as the transformation agents in methanol, the reaction provided better C-17β/C17α ratio (see entry 5 and 6 in Table 1). The best regioseletivity result was accomplished by using HCO_2Cs in MeOH at reflux for 12 h, possibly due to the novel "cesium effect" [32,50,51]. Its isomeric ratio of C-17β/C17α (**1b**/**1c**) was 98/2 and the isolated yield was 87%. For the transformation by alkali formates, the isomers C-17β/C17α (**1b**/**1c**) were also determined by the column chromatography. The ratios were shown in the entry 4–6 of Table 1. The results were consistent with the data by GC. Furthermore, we investigated the reaction of different equivalent of cesium formate (HCO_2Cs) including 1.0, 2.0, 3.0 and 5.0 equiv with α-bromoketone **1a** in dry MeOH. The reaction time would be prolonged to >24 h under the less amount of HCO_2Cs. A reliable procedure for giving the transformation products involved treatment of α-hydroxyketone substrates was the use of 3.0 equiv of HCO_2Cs in dry MeOH at reflux.

Different α-haloketones **2a**–**13a** were then allowed to react with HCO_2Cs in dry MeOH at reflux to give the corresponding α-hydroxyketones **2b**–**13b** for the investigation of the reactivity of different substrates (Scheme 2 and Table 2). For alkyl-substituted α-bromoketones **2a**, the reaction provided the desired α-hydroxyketone **2b** in high yield (94%, see Table 2). Application of same reaction conditions to 2-bromo-1-phenylethanone **3a** and 2-bromo-1-arylethanones with para-substitutents, including Me, OMe and CN groups (**4a**, **5a**, and **6a**) also gave the corresponding products **3b**–**6b** in good yields (84–92%). The new method was suitable for 2-bromo-1-(naphthalen-6-yl)ethanone **7a** and 1-(bromoacetyl)pyrene **8a**. The corresponding products **7b** and **8b** was obtained in 84% and 64%, respectively. The relatively lower yield of **8b** might due to the light-sensitivity chromophore fullerene in **8a** [52].

The synthetic strategy is also applicable to 2-chloro-*N*-(2,6-dimethylphenyl)acetamide (**9a**), 2-chloro-*N*-(1,3-diphenyl-1*H*-pyrazol-5-yl)acetamide (**10a**), *N*-bromomethylphthalimide (**11a**), and 1-(bromomethylsulfonyl)benzene (**12a**) to afford the desired transformation products **9b**–**12b** in 67–95% yields. Only the one case of bromoacetaldehyde ethylene acetal (**13a**), the reaction did not provide the corresponding product **13b**. The results indicated the essential role electron-withdrawing groups in α-carbon to the halogens, such as carbonyl, amide, imide, and sulfone groups, for the hydrolysis reaction.

3. Conclusion

A new transformation method was developed for the preparation of α-hydroxyketones from α-haloketones by using cesium formate. The synthetic strategy was also applicable to 2-chloro-*N*-(2,6-dimethylphenyl)acetamide, 2-chloro-*N*-(1,3-diphenyl-1*H*-pyrazol-5-yl)-acetamide, *N*-bromomethylphthalimide, and 1-(bromomethylsulfonyl)benzene to give the corresponding transformation products in moderate to excellent yields.

4. Experimental

4.1. General procedure

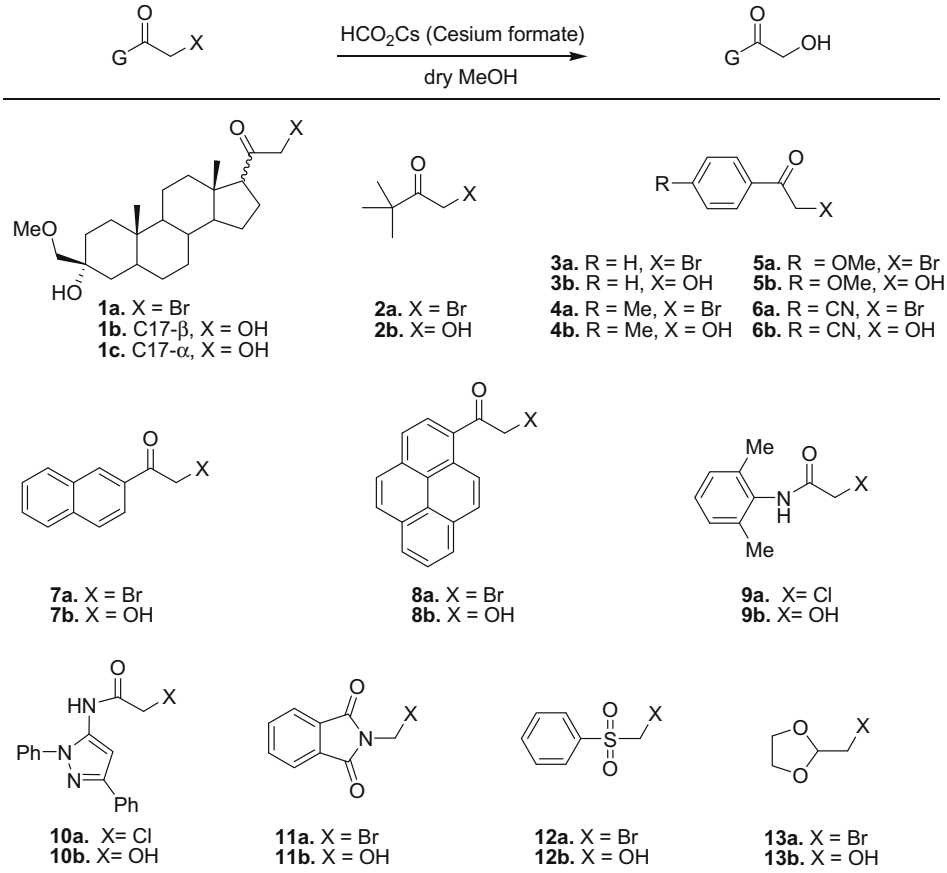
21-Bromo-3α-hydroxyl-3β-methoxymethyl-5α-pregnan-20-one (**1**) was prepared by following our published procedure [42]. Cesium formate, potassium formate, and sodium formate were purchased from Aldrich Chemical Co.

4.2. Standard procedure for the transformation of α-haloketones to α-hydroxyketones (*1b*–*12b*)

A solution of α-bromoketones (**1a**–**10a**), *N*-(bromomethyl)phthalimide (**11a**), 2-(bromomethyl)tetrahydro-2*H*-pyran (**12a**), or bromoacetaldehyde ethylene acetal (**13a**, 1.0 equiv) and cesium formate (HCO_2Cs, 3.0 equiv) in dry MeOH (10 mL) was heated at reflux for >2.0 h. When the reaction was completed, the solution was filtered to remove the excess amount of HCO_2Cs and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel or re-crystallization to give the corresponding α-hydroxyketones **1b**–**10b** and **1c** and **11b** and **12b** in 89–95% yields.

4.3. 3α-Hydroxy-21-(1′-hydroxy)-3β-methoxymethyl-5α,17β-pregnan-20-one (*1b*)

TLC R_f 0.31 (50% EtOAc in hexane); mp 126–128 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.58 (s, 3H, CH_3), 0.71 (s, 3H, CH_3), 1.16–2.42 (m, 24 H), 3.14 (s, 2H, CH_2), 3.34 (s, 3H, CH_3), 4.14 (d, 2H, J = 4.0 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 11.19, 13.57, 20.86, 22.91, 24.48, 28.34, 30.19, 31.89, 33.29, 35.50, 36.01, 37.05,



Scheme 2.

Table 2
Transformation reaction of α-bromoketones with cesium formate (HCO_2Cs).

Substrate	X	Reaction time (h)	Products	Yield (%)[a]
1a	Br	12	**1b**	87
2a	Br	2	**2b**	94
3a	Br	2	**3b**	92
4a	Br	2	**4b**	88
5a	Br	2	**5b**	85
6a	Br	2	**6b**	84
7a	Br	2	**7b**	84
8a	Br	2	**8b**	64
9a	Cl	24	**9b**	91
10a	Cl	~50	**10b**	67
11a	Br	18	**11b**	95
12a	Br	~50	**12b**	89
13a	Br	>72	**13b**	–[b]

[a] The yield was provided by the column separation.
[b] Non-detectable.

38.78, 40.15, 45.00, 53.91, 56.81, 59.32, 59.40, 69.42, 71.00, 81.89, 210.44; IR (KBr) 3431 (br, OH), 2976 (m), 2923 (m), 2839 (m), 1711 (s, C=O), 1095 (m, C–O), 1479 (m), 1368 (m), 1290 (m), 1235 (m) cm^{-1}; EIMS *m/z* (relative intensity) 347 (M – 31, 17), 334 (43), 333 (100), 301 (20), 269 (34), 109(14), 95 (23), 81 (25), 55 (19); HRMS calcd for $C_{23}H_{38}O_4$ 378.2770, found 378.2765.

4.4. 3α-Hydroxy-21-(1′-hydroxy)-3β-methoxymethyl-5α,17α-pregnan-20-one (**1c**)

TLC R_f 0.31 (50% EtOAc in hexane); mp 126–128 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.58 (s, 3H, CH_3), 0.71 (s, 3H, CH_3), 1.16–2.42 (m, 24H), 3.14 (s, 2H, CH_2), 3.34 (s, 3H, CH_3), 4.14 (d, 2H, J = 4.0 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 11.19, 13.57, 20.86, 22.91, 24.48, 28.34, 30.19, 31.89, 33.29, 35.50, 36.01, 37.05, 38.78, 40.15, 45.00, 53.91, 56.81, 59.32, 59.40, 69.42, 71.00, 81.89, 210.44; IR (KBr) 3431 (br, OH), 2976 (m), 2923 (m), 2839 (m), 1711 (s, C=O), 1095 (m, C–O), 1479 (m), 1368 (m), 1290 (m), 1235 (m) cm^{-1}; EIMS *m/z* (relative intensity) 347 (M – 31, 17), 334 (43), 333 (100), 301 (20), 269 (34), 109(14), 95 (23), 81 (25), 55 (19); HRMS calcd for $C_{23}H_{38}O_4$ 378.2770, found 378.2765.

4.5. N-(2,6-Dimethylphenyl)-2-hydroxyacetamid (**9b**)

TLC R_f 0.13 (50% EtOAc in hexane); mp 61.8–63.7 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.18 (s, 6H, CH_3), 4.19 (s, 2H, CH_2), 7.06–7.08 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.29 (2 × CH_3), 62.12, 127.58 (2 × CH), 128.23 (2 × CH), 132.80, 135.36, 170.98; IR (KBr) 3367 (br, OH), 2958 (m), 2920 (m), 1645 (s, C=O), 1593 (m), 1471 (m), 1072 (m), 769 (m), 707 (m) cm^{-1}; EIMS *m/z* (relative intensity) 179 (M^+, 50), 148 (M – 31, 100), 121 (48), 120 (34), 106 (23), 105 (28), 91 (12), 77 (16); HRMS calcd for $C_{10}H_{13}NO_2$ 179.0946, found 179.0951.

4.6. 2-Hydroxy-N-(1,3-diphenyl-1H-pyrazol-5-yl)acetamide (**10b**)

TLC R_f 0.2 (50% EtOAc in hexane); mp 164.5–166.4 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.19 (s, 2H, CH_2), 7.12 (s, 1H), 7.23–7.87 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.19, 62.19, 95.04, 124.66 (2 × CH), 125.78 (2 × CH), 128.27, 128.65 (2 × CH), 129.96 (2 × CH), 132.74, 136.09, 137.57, 152.09, 167.89; IR (KBr) 3358 (s, OH), 2922 (m), 2852 (m), 2378 (m), 2312 (m), 1708 (s, C=O), 1598 (m), 1564 (s), 1492 (m), 1460 (m), 1367 (m), 1072 (m), 956 (m), 763(m) cm^{-1}; EIMS *m/z* (relative intensity) 293

(M^+, 100), 236 (23), 235 (75), 234 (25), 207 (10), 131 (6), 102 (15), 77 (16); HRMS calcd for $C_{17}H_{15}N_3O_2$ 293.1164, found 293.1170.

4.7. 2-(Hydroxymethyl)-1H-isoindole-1,3(2H)-dione (**11b**)

TLC R_f 0.56 (50% EtOAc in hexane); mp 101.5–102.2 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.06 (s, 2H, CH_2), 7.71–7.75 (m, 2H, ArH), 7.85–7.90 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 57.37, 68.69, 123.74 (2 × CH), 131.82, 132.63, 134.42 (2 × CH), 167.96; IR (KBr) 2929 (br, OH), 1712 (s, C=O), 1683 (m), 1413 (m), 1350 (m), 1327 (m), 1165 (m), 1083 (m), 987 (m), 960 (m), 912 (m), 727 (m), 711 (m) cm^{-1}; EIMS *m/z* (relative intensity) 176 (M^+, 70), 160 (M – 17, 100), 133 (8), 117 (1), 104 (16), 76 (20), 50 (10); HRMS calcd for $C_9H_7NO_3$ 177.0426, found 177.0430.

4.8. Hydroxymethyl phenyl sulfone (**12b**)

TLC R_f 0.4 (50% EtOAc in hexane); mp 71.0–72.6 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.98 (s, 2H, CH_2), 7.49–7.58 (m, 3H, ArH), 7.84–7.88 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 44.42, 127.28 (2 × CH), 129.37 (2 × CH), 133.72, 140.50; IR (KBr) 3024 (br, OH), 2926 (m), 1583 (m), 1446 (m), 1330 (m), 1280 (m), 1147 (m), 1085 (m), 960 (m), 929 (m), 750 (m), 690 (m), 528 (m) cm^{-1}; EIMS *m/z* (relative intensity) 171 (M^+, 1), 156 (32), 141 (M – 31, 32), 125 (6), 94 (32), 77 (100), 69 (11), 57 (14), 51(27); HRMS calcd for $C_7H_8O_3S$ 172.0194, found 172.0198.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.031.

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