Primary alkanols: oxidative homocondensation in water and cross-condensation in methanol

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Water was used as a reaction medium and a reagent in oxidation of primary alkanols to dimeric esters and alkanoic acids using either molecular bromine or a hydrogen peroxide— hydrobromic acid mixture as the oxidants. The similar reaction in methanol produced methyl alkanoates.

Key words: oxidation, water, methanol, alkanols, carboxylic acids, esters, bromine, hydrogen peroxide, hydrobromic acid.

Oxidation of alkanols to aldehydes, ketones, and alkanoic acids is one of the fundamental reactions in organic chemistry widely used in science and technology and is still of academic interest. In recent years, a new approach to oxidation of primary alkanols was developed. This is oxidative condensation of primary alkanols to alkanoates without the use of the corresponding alkanoic acids as the starting reagents. This strategy was implemented in the synthesis of two type of esters, namely, methyl esters (by cross-condensation of alkanols and arylalkanols with methanol) and "dimeric" esters (by homocondensation of two molecules of the same alkanol). Synthesis of methyl alkanoates was accomplished in the presence of the following oxidizing agents: Ca(OCl)₂,¹ Bu^tOCl/pyridine², PhIO/KBr,³ I₂/K₂CO₃,⁴ TsNBr₂/ K₂CO₃,⁵ and trichloroisocyanuric acid.⁶ Methyl benzoates were synthesized by the reactions of benzylic alcohols with methanol mediated with NaIO₄/LiBr,⁷ MnO₂/NaCN,⁸ $ZnBr_2/H_2O_2$,⁹ and H_2O_2/HBr^{10} oxidizing systems. The reactions under aerobic conditions were performed with CBr₄¹¹ or catalytic systems involving Pd^{12,13}, Au¹⁴, Co¹⁵, Ru,¹⁶ and Ir¹⁷ in the presence of hydrogen acceptor instead of the oxidizing agent. In the reactions with benzylic alcohols, not only methanol was used but also other esterifying alcohols^{12–14,15,18} and N-hydroxysuccinimide.¹⁹

Cross-condensations of alkanols to give dimeric esters have been carried out in the presence of redox catalysts (mediators) in the reaction media consisting of water/ water-miscible organic solvent. The oxidizing systems were NaBrO₃-HBr,²⁰ H₂O₂-HBr,²¹ oxone-NaBr,²² oxone-NaCl,²³ H₂O₂-KBr-PhSO₃H,²⁴ and PhI(OAc)₂-KBr in ethyl acetate,²⁴ pyridinium chromate-Al₂O₃ (solventfree),²⁶ pyridinium hydrobromide perbromide in water.²⁷ In our research group, dimeric esters have been synthesized by oxidation of alkanols with $Pb(OAc)_4$ -MHal²⁸ and $Ce(NH_4)_2(NO_3)_6$ -LiBr²⁹ using mechanochemical activation, as well as with $Ce(SO_4)_2$ -LiBr in water.³⁰

It is of note that the role of water in the homo- and cross-condensations of alkanols has not been yet discussed in detail. However, water strongly affects these processes: the oxidations in pure water and in the dispersion water alkanol proceed in different directions and with different selectivities.

In the present work, we evaluated the role of water as both a reaction medium and a reagent in oxidation of primary alkanols to alkanoic acids and alkanoates. Oxidation was mediated by either molecular bromine or a hydrogen peroxide—hydrobromic acid system as a source of bromine.

Results and Discussion

Oxidation with molecular bromine. In the present work, we pioneered in using molecular bromine as a stoichiometric reagent for selective homo- and cross-coupling of primary alkanols **1a**—**h**. Treatment of solutions of primary alkanols **1b**,**c**,**e**,**g** in methanol with bromine yielded methyl esters **2b**,**c**,**e**,**g** (Scheme 1, Table 1).



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Table 1. Oxidation of alkanols with bromine in methanol^a

Entry	Alkanol	Molar ratio 1 : Br ₂	t∕°C	Conversion of 1 (%)	$\operatorname{Yield}^{b}(\%)$
1	1b	1:4	20	47	2b , 90
2	1b	1:4	40	65	2b , 93
3	1c	1:2.5	20	61	2c , 95
4	1c	1:2.5	40	83	2c , 95
5	1c	1:4	20	75	2c , 94
6	1c	1:4	40	94	2c , 93
7	1e	1:2.5	20	71	2e , 96
8	1e	1:2.5	40	82	2e , 94
9	1e	1:4	20	89	2e , 95
10	1e	1:4	40	98	2e , 95
11	1g	1:2.5	20	65	2g , 97
12	1g	1:2.5	40	82	2g , 95
13	1g	1:4	20	83	2g , 96
14	1g	1:4	40	96	2g , 96

^{*a*} Reaction conditions: **1** (1 mmol), MeOH (4 mL), 18–20 h. ^{*b*} Conversion of compound **1** and yields of products **2** and **3** (RCOOCH₂R) were determined by GC using internal standard. Yields are calculated on the basis of the converted alkanol **1**. Yields of compounds **3b**,**c**,**e**,**g** were ~1–2%.

Conversions of alkanols 1c,e,g at 40 °C for 18-20 h at a reagent molar ratio $1: Br_2 = 1:4$ were 94–98% and show a decrease (up to $\sim 90\%$) with a decrease in the reaction temperature (to 20 °C). These conditions are optimal for the synthesis of methyl esters 2. The only exception is butan-1-ol (1b), whose conversions were 65-47% depending on the reaction temperature. The reaction performed with 1.6-fold less amount of bromine (from 4 to 2.5 mol per 1 mol of alkanol) proceeds with a 1.2-fold reduced conversion (see Table 1, cf. entries 4 and 6, 8 and 10, 12 and 14). The amount of bromine exceeding the stoichiometric value is consumed in the side reaction, namely, in oxidation of methanol. It is of note that under all oxidation conditions the yields of methyl esters 2b,c,e,g were above 90%. Due to the large excess of methanol over alkanols **1b,c,e,g** (125:1), the yields of dimeric esters (RCOOCH₂R) **3b**,c,e,g were very low (see Table 1).

At the same time, oxidation of alkanols 1c,e,g in water (Scheme 2, Table 2, entries 5–8, 17, and 18) produces esters 3c,e,g in high yields and selectivity.

Surprisingly, alkanoic acids were obtained only in trace amounts. This is especially characteristic of acids **4e**,**g**,

Table 2. Oxidation of alkanols with bromine in water and water-methanol solution^a

Entry	Alkanol	Molar ratio 1 : Br ₂	Solvent	Conversion of 1 (%)	$\operatorname{Yield}^{b}(\%)$		
					2	3	4
1	1a	1:2.5	H ₂ O	60	_	_	4 a, 95
2	1a	1:4	H ₂ O	87	_	_	4a , 96
3	1b	1:2.5	H ₂ O	76	_	3b , 17	4b , 76
4	1b	1:4	H ₂ O	89	_	3b , 8	4b , 87
5	1c	1:2.5	H ₂ O	92	_	3c , 87	4c , 11
6	1c	1:4	H ₂ O	96	_	3c , 84	4c , 15
7	1e	1:2.5	H ₂ O	98	_	3e , 96	$4e^{c}$
8	1e	1:4	H ₂ O	99	_	3e , 93	$4e^{c}$
9	1e	1:2.5	$H_2O-MeOH$ (1:1)	95	2e , 94	3e , 2	4e ^{<i>c</i>}
10	1e	1:4	$H_2O-MeOH$	97	2e , 92	3e , 4	4e ^{<i>c</i>}
11	1e	1:2.5	$H_2O-MeOH$	97	2e , 40	3e , 55	4e ^{<i>c</i>}
12	1e	1:4	$H_2O-MeOH$	99	2e , 38	3e , 53	4e ^{<i>c</i>}
13	1e	1:2.5	$H_2O-MeOH$	96	2e , 27	3e , 67	4e ^{<i>c</i>}
14	1e	1:4	$H_2O-MeOH$ (10:1)	98	2e , 21	3e , 70	4e ^{<i>c</i>}
15	1e	1:2.5	$H_2O-MeCN$	95	—	3e, 71	4e , 26
16	1e	1:4	$H_2O-MeCN$	99	—	3e , 37	4e , 60
17	1g	1:2.5	H ₂ O	96	_	3 g. 97	$4g^c$
18	1g	1:4	H ₂ O	98	—	3g , 94	$4\mathbf{g}^c$

^{*a*} Reaction conditions: **1** (1 mmol), solvent (4 mL), 18–20 h, 20 °C.

^b Conversion of compound **1** and yields of products **2**, **3**, and **4** were determined by GC using internal standard. Yields are calculated on the basis of the converted alkanol **1**.

^c Yield was $\sim 1-3\%$.

i.e., water does not participate in oxidations carried out in water as a solvent. This fact can be explained by different types of the oxidation media. In methanol, the reaction proceeds in homogeneous solution; while in water, the reaction takes place in dispersion containing water and water-insoluble aggregated alkanol particles. Vigorous stirring of the reaction mixture results in formation of the emulsion and drops of alkanols. Alkanols are oxidized to dimeric esters inside of the aggregated particles; the oxidation involves formation of aldehyde, acid bromide, and its subsequent alcoholysis^{2,7,10,21} (another plausible mechanism involves formation and oxidation of hemiacetal^{3,4}). Alkanols can react with water only on the surface of these particles to give alkanoic acids in yields not exceeding 1-2%. In contrast to alkanols **1b**,**c**,**e**,**g**, propan-1-ol (**1a**) is sufficiently miscible with water; consequently, the oxidation proceeds in the homogeneous water-propanol solution. This process results selectively in propionic acid (4a), no dimeric propyl propionate (3a) is detected (Scheme 3, see Table 2). In this case, water is not only solvent, but also plays a role of reagent actively participating in hydrolysis of propionyl bromide.

Scheme 3 Me $\rightarrow OH \xrightarrow{Br_2} Me \rightarrow O \xrightarrow{Br_2} -2 HBr Me \rightarrow O \xrightarrow{-2 HBr} Me \xrightarrow{-HBr} Me \xrightarrow{-HBr} Me \xrightarrow{-HBr} Me \xrightarrow{-HBr} Me \xrightarrow{-HBr} He \xrightarrow{-HBr}$

Butan-1-ol (**1b**) is poorly water soluble (7.9 g per 100 mL of water at 20 °C), but this is enough to cause the oxidation of **1b** predominantly in solution to give butyric acid (**4b**) with small traces of butyl butyrate (**3b**) (see Table 2). Pentan-1-ol (**1c**) is soluble in water in lesser extent (~2.7 g per 100 mL of water at 20 °C); therefore, its reaction produces pentanoic acid (**4c**) in 11–15% yield with the major product (84–87%) being pentyl pentanoate (**3c**).

The effects of a reaction medium are clearly seen not only for the reactions carried out in water but also in water—methanol solution (see Table 2, entries 9-14). Using heptan-1-ol (**1e**) as an example, it was shown that the use of a homogeneous solution containing equal amounts of water and methanol favored highly selective formation of methyl ester 2e (see Table 2, entries 9 and 10). As methanol content decreases, the solution turns into two phases (see Table 2, entries 11-14). However, not all heptan-1ol (1e) forms the dispersed phase, some amount of 1e is present in continuous phase (water—methanol). Under these conditions, despite a 50-fold molar excess of methanol relative 1e (entries 13 and 14), heptan-1-ol 1e oxidizes mostly to dimeric ester 3e and in lesser extent to methyl ester 2e. As expected, oxidation of 1e in a homogeneous solution H₂O—MeCN follows two directions producing

both dimeric ester **3e** and heptanoic acid **4e** (see Table 2,

entries 15 and 16). Oxidation with hydrogen peroxide—hydrobromic acid. Bromine is an efficient, convenient, and easy to use oxidizing agent for alkanols; however, its application for the synthesis of esters leads to side-reactions giving large amounts of hydrogen bromide. Taking this fact into account, we elaborated another approach to methyl esters and dimeric esters, which is more economically favorable and more attractive from the viewpoint of green chemistry. Hydrogen peroxide was chosen as a stoichiometric oxidizing agent and hydrobromic acid was chosen as a redox catalyst. Oxidation of alkanols 1d-g under optimum conditions in MeOH results in methyl esters 2d-g in the yields up to 93% (Table 3, entries 3, 4, 6, and 8). Similarly to oxidation with bromine, it is more difficult to oxidize butan-1-ol (1b) even under these conditions. The reaction starts from generation of bromine from hydrobromic acid, then both oxidation of alkanols and regeneration of bromine from a newly formed HBr molecules occur in the repeating cycles. Syntheses of methyl esters are shown on Scheme 4 and are summarized in Table 3.



Scheme 4



1, 2: $R = C_5 H_{11}$ (**d**), EtCH(Me)CH₂ (**h**)

Along with methyl esters, the reaction produces dimeric esters and alkanoic acids but in noticeably lower yields. The product ratio depends on both the reagent ratio and the water solubility of alkanols. The oxidation procedure involves portionwise addition of hydrogen peroxide at a uniform rate to a stirred solution of alkanol and hydrobromic acid in methanol. During first hours of the reaction, the mixture is homogeneous containing a large amount of methanol; these conditions favor formation of

Table 3. Oxidation of alkanols 1 with $HBr-H_2O_2$ in methanol^a

Table 4. Oxidation of alkanols 1 with $HBr-H_2O_2$ in water and water-methanol solution^{*a*}

Entry	Alkanol	Conversion of 1 (%)	$\operatorname{Yield}^{b}(\%)$			
			2	3	4	
1	1b	65	2b , 65	_	4b , 32	
2	1c	90	2c , 77	$3c^d$	4c , 22	
3	1d	88	2d, 89	3d ^d	4 d, 9	
4	1e	83	2e , 91	3e , 3	4 e, 4	
5^c	1e	98	2e , 80	3e , 15	4e , 3	
6	1f	90	2f , 92	3f , 7	$4\mathbf{f}^d$	
7 ^c	1f	98	2f , 79	3f , 19	$4\mathbf{f}^d$	
8	1g	92	2g , 93	3 g, 4	$4g^d$	
9°	1g	98	2g , 81	3g , 17	$4\mathbf{g}^d$	
10	1h	80	2h , 86	3h , 12	4h ^d	

^{*a*} Reaction conditions: **1** (1 mmol), reagent ratio is **1** : HBr : $H_2O_2 = 1 : 1.5 : 10$, MeOH (3 mL), 7–9 h, 65–70 °C.

^b Conversion of compound 1 and yields of products 2, 3, and 4 were determined by GC using internal standard. Yields are calculated on the basis of the converted alkanol 1.

^c MeOH (2 mL).

^d Yield was $\sim 1-2\%$.

methyl esters. For instance, 4 h after the reaction onset (see Table 3, entry 8) the molar ratio of esters 2e : 3e was 24; whereas after completion of the reaction (9 h after the reaction onset), 2e : 3e was 4. As the reaction goes to completion, the increase in the water content makes the reaction mixture cloudy and partially two-phase thus leading to the formation of dimeric esters. This explanation is in agreement with the results of the experiments 4, 6, 8 and 5, 7, 9 (see Table 3). Note that the methanol content in experiments 5, 7, and 9 was decreased 1.5-fold. A decrease in the content of methanol in the reaction mixture causes formation of a two phase dispersion, which favors the dimeric ester formation. As a result, the yield of the dimeric esters increases from 3-7% to 15-19%. Alkanols dissolved in water phase are oxidized to alkanoic acids.

In contrast to oxidation in methanol, upon aqueous oxidation of alkanols 1e-g the two-phase system is formed immediately after the reaction onset. Under these conditions, alkanols nearly quantitatively produce the corresponding dimeric esters 3e-g (Table 4). Addition of acetonitrile destroys two phase system water—heptan-1-ol (1e); as a result, oxidation occurs in homogeneous medium giving

Entry	Alkanol	Solvent	Conversion	Yield ^{<i>b</i>} (%)		
			of 1 (%)	2	3	4
1	1a	H ₂ O	60	_	_	4a , 96
2	1b	H ₂ O	82	_	3b , 10	4b , 88
3	1b	H ₂ O-MeOH	[60	_	3b , 3	4b , 95
		(5:1)				
4	1e	H ₂ O	98	_	3e , 86	4e , 12
5 ^c	1e	H ₂ O	80	_	3e , 99	_
6	1e	H ₂ O-MeCN	95	_	3e , 24	4e , 73
		(1:9)				
7	1e	H ₂ O-MeOH	[93	2e , 7	3e , 89	4e , 2
		(5:1)			-	
8	1e	H ₂ O-MeOH	I 96	2e , 12	3e , 83	4e , 3
		(5:2)		-		ĺ.
9	1e	H ₂ O-MeOH	[98	2e , 45	3e , 50	4 e, 4
		(1:1)				
10	1f	H ₂ O	98	_	3f , 90	4f , 7
11	1f	H ₂ O-MeOH	[93	2f , 7	3f , 91	_
		(5:1)				
12	1g	H ₂ O	98	_	3 g, 96	4g , 2
13	1g	H ₂ O-MeOH	I 95	2g , 8	3 g, 90	_
	U	(5:1)		0	0,	

^{*a*} Reaction conditions: 1 (1 mmol), reagent ratio is 1 : HBr : H_2O_2 = 1 : 1.5 : 10, solvent (5 mL), 7–9 h; 65–70 °C.

^b Conversion of compound **1** and yields of products **2**, **3**, and **4** were determined by GC using internal standard. Yields are calculated on the basis of the converted alkanol **1**.

^c Reagent ratio was $1e : HBr : H_2O_2 = 1 : 1.5 : 5$.

heptanoic acid **4e** as a major product instead of dimeric ester **3e**, the product ratio **4e** : **3e** being 3:1 (Scheme 5; see Table 4, entry 6). In these cases, water actively participates in the reaction.

Aqueous oxidation of propan-1-ol (1a) and butan-1-ol (1b) with the H_2O_2 —HBr system proceeds analogously to oxidation with bromine: compound 1a gives selectively propionic acid (4a), compound 1b produces butanoic acid (4b) and butyl butyrate (3b) in a ratio of ~9 : 1 (see Table 4, entries 1 and 2).

Alkanols **1e**—**g** are oxidized in the water—methanol (5 : 1) solution in two phase system. Under these conditions, similarly to oxidation with bromine, despite a 50-fold



excess of MeOH relative to 1e-g, the yields of dimeric esters 3e-g exceed by one order of magnitude those of methyl esters 2e-g (see Table 4, entries 7, 11, and 13).

An increase in the methanol content (H_2O : MeOH = = 5 : 2, see Table 4, entry 8) does not virtually effect the outcome of oxidation of alkanol **1e**. At H_2O : MeOH = = 1 : 1, the dispersion phase is partially destroyed and oxidation follows two directions affording two esters (**2e** and **3e**) in nearly equal amounts (see Table 4, entries 8 and 9). A divergence in the reaction outcome between experiments 8 and 9 from Table 4 and experiments 9 and 10 from Table 2, which were carried out at the same ratio MeOH : H_2O (1 : 1), can be explained by actually higher content of water in experiments 8 and 9 from Table 4 due to the use of aqueous solutions of hydrogen peroxide and hydrobromic acid.

¹H NMR spectra of methyl (2) and dimeric (3) esters exhibit signals characteristic of these molecules: at $\delta 2.3-2.4$ (t, CH₂COO) and 3.5-3.6 (s, C(O)OCH₃) for 2; at $\delta 2.3-2.4$ (t, CH₂COO) and 4.0-4.1 (t, C(O)OCH₂) for 3. ¹³C NMR spectra contain signal of the C=O group carbon atoms at $\delta 171-174$.

In summary, formation of the disperse medium is a decisive factor promoting oxidative homocondensation of primary alkanols in water. Destruction of the dispersion by adding acetonitrile leads to oxidation in homogeneous solution giving predominantly alkanoic acids. Water soluble alkanols producing homogeneous solutions are oxidized to alkanoic acids, formation of dimeric esters under these conditions was not detected. In methanol, alkanols are oxidized to methyl esters; in water-methanol mixture they produce alkanoic acids, methyl and dimeric esters in the ratio depending on both the water solubility of alkanols and the water : methanol ratio. Oxidative homocondensation of alkanols and cross-coupling with methanol upon treatment with bromine were taken as the basis for elaboration of the simple and versatile preparative procedures towards dimeric and methyl esters of alkanoic acids.

Experimental

GC analysis was performed on a Chrom-5 chromatograph with the flame-ionization detector and 3000×3 mm analytical glass columns with 5% SE-30 and 5% FFAP on Chromaton N-AW-HMDS (0.16–0.20 mm). The product yields were determined by an internal standard method with the empirical correlation coefficients. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer for the neat samples. ¹H and ¹³C NMR spectra were recorded on a Bruker AC-200 instrument in CDCl₃ using standard procedures. The reaction products were isolated by column chromatography (silica gel L, 40/100 μ m, elution with heptane–ethyl acetate). The stating propan-1-ol (**1a**), butan-1ol (**1b**), pentan-1-ol (**1c**), hexan-1-ol (**1d**), heptan-1-ol (**1e**), octan-1-ol (**1f**), nonan-1-ol (**1g**), and 3-methylpentan-1-ol (**1h**) available from Acros Organics were distilled prior to use. Hydrogen peroxide (35% aqueous solution, pure grade) and bromine (99%+) available from Acros Organics were used as purchased. Hydrobromic acid (48% aqueous solution, pure grade) was used without additional purification.

Bromine-mediated oxidation of primary alkanols 1a—h in methanol (general procedure). A mixture of alkanol 1 (1 mmol) and MeOH (4 mL) was vigorously stirred with bromine at 20 °C (or 40 °C) for 18–20 h (the reagent molar ratios are given in Table 1). After completion of the reaction indicated by a color change of the reaction mixture from red to light-orange, water (10–15 mL) was added and the mixture was extracted with diethyl ether ((3×20 mL). The combined organic layers were washed with saturated aqueous NaHCO₃ (10–15 mL), water (10–15 mL), dried with MgSO₄, and the solvent was removed *in vacuo*. The conversions of the starting alkanols and the product yields were determined by GC using an internal standard.

Bromine-mediated oxidation of primary alkanols 1a—h in methanol—water (general procedure). A mixture of alkanol 1 (1 mml) and a methanol—water mixture (4 mL) was vigorously stirred with bromine at 20 °C for 19–20 h (the reagent molar ratios are given in Table 2). Then water (10–15 mL) was added, the mixture was extracted with diethyl ether (3×20 mL). The combined organic layers were washed with water (2×15 mL), dried with MgSO₄, and the solvent was removed *in vacuo*. The conversions of alkanols and the product yields were determined by GC.

Oxidation of primary alkanols 1a—h with H_2O_2 —HBr in methanol or in a water—methanol mixture (general procedure). To a vigorously stirred solution of alkanol 1 (1 mmol) in 48% HBr in MeOH or MeOH—H₂O, a solution of H_2O_2 (35%) in the corresponding solvent (1—1.5 mL) was added by portions (0.2—0.25 mL) at 65—70 °C (the reagent molar ratios are given in Tables 3 and 4). After addition of the first portion of the H_2O_2 solution, the reaction mixture turned to light yellow and after 20—30 min was colorless. Then the next portion of hydrogen peroxide was added. After completion of the reaction, the mixture was cooled, extracted with diethyl ether (3×15 mL), the combined organic layers were washed with water, dried with MgSO₄, and the solvent was removed *in vacuo*. The conversions of alkanols and the product yields were determined by GC.

The structures of all synthesized compounds 2, 3, and 4 were confirmed by ¹H and ¹³C NMR spectroscopy and IR spectroscopy. The products were isolated by silica gel column chromatography.

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