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OXIDATIVE CLEAVAGE OF 1, 2-DIOLS, α-KETOLS AND 1, 2-DIKETONES WITH AQUEOUS SODIUM HYPOCHLORITE

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OXIDATIVE CLEAVAGE OF 1,2-DIOLS, α-KETOLS AND 1,2-DIKETONES WITH AQUEOUS SODIUM HYPOCHLORITE

Submitted by (08/01/06)

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The oxidative cleavage of 1,2-diols has diverse applications in organic synthesis. Though oxidants such as aqueous hydrogen peroxide-tungstate or phosphate,[1] N-iodosuccinimide,[2] NBS-tetra(*n*-butyl)ammonium iodide,[3] Jones reagent,[4] chromic acid[5] have been reported, the reagents most often used to cleave 1,2-diols are periodic acid and lead tetracetate.[6] Periodic acid is primarily used for degradation of water-soluble diols while lead tetraacetate is used mainly for water-insoluble diols. There are limitations and difficulties like cost factor, reaction conditions and troublesome workup concerning cleavage of 1,2-diols with these and other reagents.[1,5c] The search for a practical and efficient reagent for C-C bond cleavage of a variety of 1,2-diols, α-ketols and 1,2-diketones has been the focus of our interest. We have described different applications of aqueous sodium hypochlorite.[7-10] This paper reports a simple, convenient and inexpensive procedure for the oxidative cleavage of water soluble and water insoluble 1,2-diols, α-ketols and 1,2-diketones with aqueous sodium hypochlorite in acetonitrile at ambient temperature. The results are described in *Table 1*.

Various 1,2-diaryl- and dialkyl-1,2-diols (**1a-1l**) underwent oxidative cleavage with aqueous sodium hypochlorite to give the corresponding carboxylic acids when a 1:20 molar ratio of substrate to NaOCl (**2a-2j**) (*Entries 1-10*) was used. The oxidative cleavage of 1,2-diols can be controlled to give the corresponding aldehydes or ketones as the major product using 1:10 molar ratio (substrate: NaOCl) (*Entries 11-19*). 2,3-Diaryl-2,3-butanediols also underwent oxidative cleavage under these conditions to give rise to the corresponding carboxylic acids in high yields (**2m-2p**) (*Entries 20-23*). It was confirmed by monitoring the reactions of 1,2-diols as well as by independent reactions of aldehydes and acetophenone with aqueous sodium hypochlorite at ambient temperature that the formation of carboxylic acids presumably proceeds *via* the aldehydes and ketones. The 1,2-diols employed for oxidative cleavage were invariably a mixture of *meso*-and *dl*-isomers and subsequent oxidative cleavage of *meso*- and of *dl*-hydrobenzoin did not show any noticeable change in the ratio of products. Benzopinacoles (**1q-1s**) underwent oxidation under similar conditions to give benzophenones (*Entries 24-26*). These results are reported in *Table 1*.

Table 1. Oxidation of 1,2-Diols, α-Ketols and 1,2-Diketones in Acetonitrile.[a,b]

Entry	Substrate	Molar ratio	Time (h)		% Yield	
				RCO_2H,	m.p, obs (*lit.*)	RR'CO/ Ar_2CO
1	*1a*	1:20	4.5	83(**2a**)	120°C(121°C)	----
2	*1b*	1:20	3.0	93(**2b**)	103°C(103°C)	----
3	*1c*	1:20	3.5	86(**2c**)	183°C(182-185°C)	----
4	*1d*	1:20	3.5	87(**2d**)	98°C(98°C)	----
5	*1e*	1:20	3.0	88(**2e**)	238°C(239°C)	----
6	*1f*	1:20	3.0	89(**2f**)	155°C(155°C)	----
7	*1g*	1:20	3.5	88(**2g**)	229°C(121°C)	----
8	*1h*	1:20	18	89(**2h**)	161°C(160-162°C)	----
9	*1l*	1:20	1.5	88(**2i**)	----	----
10	*1j*	1:20	2.0	84(**2j**)	----	----
11	*1a*	1:10	0.5	27(**2a**)	----	63(**3a**)
12	*1b*	1:10	1.5	4(**2b**)	----	78(**3b**)
13	*1c*	1:10	0.25	22(**2c**)	----	73(**3c**)
14	*1e*	1:10	0.5	15(**2e**)	48°C(47-50°C)	81(**3e**)
15	*1h*	1:10	0.25	2(**2h**)	----	84(**3h**)
16	*1i*	1:10	0.25	2(**2i**)	----	83(**3i**)
17	*1j*	1:10	0.25	----	----	83(**3j**)
18	*1k*	1:10	0.5	12(**2k**)	----	84(**3k**)
19	*1l*	1:10	2.0	16(**2l**)	44°C(42-45°C)	71(**3l**)
20	*1m*	1:20	1.5	87(**2m**)	238°C(238-239°C)	----
21	*1n*	1:20	5.0	85(**2n**)	181°C(180-182°C)	----
22	*1o*	1:20	5.0	86(**2o**)	183°C(182-185°C)	----
23	*1p*	1:10	0.5	88(**2p**)	120°C (121°C)	----
24	*1q*	1:20	8.0	----		82(**3q**) 48°C(48°C)
25	*1r*	1:20	8.0	----		88(**3r**) 81°C(82°C)
26	*1s*	1:20	4.0	----		92(**3s**)144°C(144°C)
27	*4a*	1:15	2.5	85(**5a**)	120°C (121°C)	----
28	*4b*	1:15	5.0	85(**5b**)	180°C (180-182°C)	----
29	*4c*	1:15	2.0	86(**5c**)	238°C (238-239°C)	----
30	*4d*	1:15	1.0	88(**5d**)	----	----
31	*4e*	1:15	1.0	86(**5e**)	----	----
32	*6a*	1:10	0.5	87(**7a**)	120°C(121°C)	----
33	*6b*	1:10	1.0	84(**7b**)	180°C(180-182°C)	----
34	*6c*	1:10	1.5	85(**7c**)	161°C(160-162°C)	----
35	*6d*	1:10	1.5	79(**7d**)	----	----
36	*6e*	1:10	1.5	83(**7e**)	----	----

a) 30 mL of acetonitrile was used per 1g of substrate in all the reactions. b) At ambient temperature

$$\underset{\textit{1a-s}}{\mathrm{RR'C(OH)C(OH)RR'}} \xrightarrow[\mathrm{CH_3CN,\ r.t}]{\mathrm{aq.\ NaOCl}} \underset{\textit{2a-p}}{\mathrm{RCOOH}} + \underset{\textit{3a-c, e, h-l, q-s}}{\mathrm{RR'CO}} \qquad (1)$$

a) R = C_6H_5, R' = H
b) R = 2-$CH_3C_6H_4$, R' = H
c) R = 4-$CH_3OC_6H_4$, R' = H
d) R = 2-$CH_3OC_6H_4$, R' = H
e) R = 4-ClC_6H_4, R' = H
f) R = 3-BrC_6H_4, R' = H
g) R = Piperonyl, R' = H
h) R = 1-Naphthyl, R' = H
i) R = *n*-C_3H_7, R' = H
j) R = *n*-C_2H_5, R' = H
k) R = 4-$CH_3C_6H_4$, R' = H
l) R = Veratryl, R' = H
m) R = 4-ClC_6H_4, R' = CH_3
n) R = 4-$CH_3C_6H_4$, R' = CH_3
o) R = 4-$CH_3OC_6H_4$, R' = CH_3
p) R = C_6H_5, R' =CH_3
q) R = R' =C_6H_5
r) R = 4-BrC_6H_4, R' =C_6H_5
s) R = R' = 4-ClC_6H_4

We also report herein oxidative cleavage of α-ketols (benzoins and acyloins) (**4a-4e**) with aqueous sodium hypochlorite using 1:15 molar ratio (substrate: NaOCl) at ambient temperature to give carboxylic acids (*Eq. 2*) in high yields (*Entries 27-31*). When reactions of

$$\underset{\textit{4a-e}}{\mathrm{RCH(OH)COR}} \xrightarrow[\mathrm{CH_3CN,\ r.t}]{\mathrm{aq.\ NaOCl}} \underset{\textit{5a-e}}{\mathrm{RCOOH}} \qquad (2)$$

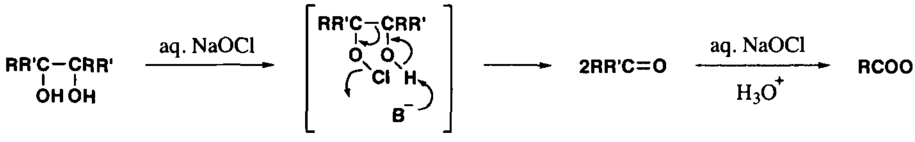
a) R = C_6H_5 b) R = 4-$CH_3C_6H_4$ c) R = 4-ClC_6H_4 d) R = *n*-C_3H_7 e) R = *n*-C_2H_5

α-ketols were carried out using lower molar ratio of NaOCl, small amounts of aldehydes were also formed. Similarly, 1,2-diaryl-and 1,2-dialkyl-1,2-diketones (**6a-6e**) underwent complete oxidative cleavage with aqueous sodium hypochlorite using 1:10 molar ratio in acetonitrile at ambient temperature to give the corresponding carboxylic acids (*Entries 32-36*) (*Eq. 3*) (*Table 1*)

$$\underset{\textit{6a-e}}{\mathrm{RCOCOR}} \xrightarrow[\mathrm{CH_3CN,\ r.t}]{\mathrm{aq.\ NaOCl}} \underset{\textit{7a-e}}{\mathrm{RCOOH}} \qquad (3)$$

a) R = C_6H_5 b) R = 4-$CH_3C_6H_4$ c) R = 1-Naphthyl d) R = *n*-C_3H_7 e) R = *n*-C_5H_{11}

Moreover, the oxidative cleavage of 1,2-diols *via* α-ketols and 1,2-diketones has been ruled out by monitoring independent reactions of hydrobenzoin using lower molar ratio of sodium hypochlorite. The oxidative cleavage is proposed plausibly proceed *via* hypochlorites, followed by carbon-carbon bond cleavage to give aldehydes/ketones, which undergo subsequent oxidation with hypochlorite to give carboxylic acids (*Scheme 1*). α-Ketols and 1,2-diketones also undergo oxidative cleavage in an analogous manner. R'COOH is not formed in the cases wherein acetophenones are the intermediates in a manner analogous to iodoform reaction of acetophenones. However, hydrobenzoin dimethylether did not undergo reaction with aq. sodium hypochlorite in agreement with the proposed mechanism, shown below.



EXPERIMENTAL SECTION

Acetonitrile (E. Merck) was used in all the reactions. Sodium hypochlorite solution, 1.082 M, (E. Merck) or prepared in the laboratory by a reported method[11] was used. Hydrobenzoins were prepared by reductive coupling of aldehydes by Al-KOH.[12] Aliphatic 1,2-diols were prepared by hydroxylation of corresponding olefins.[13] Acyloins were prepared *via* the acyloin condensation[14] and 1,2-diketones were synthesized from 1,2-diols using NBS.[15]

General Procedure for 1,2-Diols.- To a solution of 0.2 g (0.935 mmol) of hydrobenzoin in 6 mL of acetonitrile in a 50 mL round-bottomed flask equipped with a stir bar was added 8.62 mL (9.345 mmol) of 1.082 M sodium hypochlorite solution and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC, using petroleum ether: ethyl acetate (90:10) as eluent. The reaction mixture was quenched with water (~15 mL) and acidified with conc. HCl. The product was than extracted with diethyl ether (3 x 10 mL). The combined ethereal extract was dried over anhydrous $MgSO_4$ and the ether was removed under reduced pressure to give benzoic acid (83%).

In reactions with lower molar ratios of the reagent (*Entries 11-19*), the reaction mixture was first extracted with dichloromethane (3 x 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated. After drying under vacuum, the aldehyde was characterized *via* IR and NMR spectra. The aqueous layer was acidified with conc. HCl until acidic and the carboxylic acid was isolated as mentioned above. Whereas, in the reactions of aliphatic 1,2-diols, the product was extracted with diethyl ether (3 x 10 mL) without quenching with water to isolate any aldehyde formed as done previously. The product(s) were identified by mp., mixed mp. (wherever applicable), IR and NMR spectra, respectively.

General Procedure for α-Ketols and 1,2-Diketones.- To a solution of benzoin (0.2 g 0.943 mmol) in 6 mL of acetonitrile in a 50 mL round-bottomed flask equipped with stir bar was added 7.7 mL (9.431 mmol) of 1.082 M sodium hypochlorite and the reaction mixture was stirred magnetically at room temperature. The progress of the reaction was monitored by observing the disappearance of benzoin by TLC (eluent: petroleum ether-ethyl acetate: 90:10). The reaction mixture was quenched with water and acidified with conc. HCl until acidic. The carboxylic acids were isolated as in above procedure and identified as above.

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