Oxidative Deoximation with Sodium Hypochlorite

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A simple and convenient procedure for the deoximation with 0.5 M aqueous hypochlorite at ambient temperature is reported. Ketoximes yielded ketones quantitatively and aldoximes yielded aldehydes only at pH 5—7 or mixture of aldehydes and carboxylic acids at pH 10—11.

Regeneration of carbonyl compounds from stable and readily prepared ketoximes and aldoximes has received attention in recent years.[1a,1b,1c] Since oximes can be prepared from non-carbonyl compounds, the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. However, many of these methods to regenerate carbonyl compounds involve reagents which are either expensive or not readily available.[1d—o] We became interested in the regeneration of carbonyl compounds because of our experience with sodium hydpochlorite, an inexpensive versatile reagent.[2] It has been employed in the oxidation of side chains of aromatic rings,[3] oxidation of α-amino acids,[4] epoxidation of 1,4-naphthoquinone and benzylidenacetophenone,[5] regeneration of carbonyl compounds from tosyl hydrazones,[6] oxidation of alcohols,[7] and the oxidation of benzylic halides to carbonyl compounds.[2]

In this communication we report a simple and convenient procedure for the deoximation of ketoximes and aldoximes with sodium hypochlorite (0.5 M, 1 M=1 mol $\mathrm{dm^{-3}}$) at ambient temperature. The reactions were observed to be complete in 15 to 30 min using 10 equimolar amount sodium hypochlorite in acetonitrile as monitored by disappearance of starting material by thin layer chromatography (TLC). Whereas ketones were obtained in high yields, aldoximes gave a mixture of the corresponding aldehydes and carboxylic acids in various amounts depending upon reaction time and ratio of aldoximes to sodium hypochlorite when the reactions were carried out at pH 10—11. However, quantitative deoximation of the aldoximes to aldehydes were observed when the reactions were carried out at pH 5—7 using buffer solution of pH 4.

Several examples are shown in Tables 1 and 2 and can be generalized as follows (Scheme 1):

An interesting feature of the reactions of aldoximes is that the ratio of the products is dependent on the molar ratio of the oxime vs. sodium hypochlorite. Significantly larger amounts of carbonyl compounds are formed with lower concentration of the reagent. When the reaction was carried out in an acidic medium (pH 5—7) using a buffer solution of pH 4, there was almost exclusive formation of carbonyl compound and no carboxylic acid was detected. It was also revealed that the formation of carboxylic acid is taking place directly from the oxime and is not a result of rapid oxidation of the aldehyde produced initially which was confirmed by the blank reaction of benzaldehyde with sodium hypochlorite in 1 : 10 molar ratio for 15 min. Acetophenone oxime gave benzoic acid besides acetophenone (Runs 9—11) due to competing haloform reaction. However, when the reaction was done at pH 5—7, only acetophenone was obtained (Run 12). This is in agreement with the fact that haloform reaction takes place only in alkaline medium.

The possibility that the deoximation is caused by sodium hydroxide was eliminated as no benzophenone was detected when benzophenone oxime (**1a**) was treated with 10% sodium hydroxide for 60 min. The intermediate of this reaction is estimated to be an organic hypochlorite.

Experimental

Melting points were measured on a Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on Perkin–Elmer model 621 and Shimadzu model 435 spectrophotometer. NMR spectra were recorded on Perkin–Elmer R-32 90 MHz and Hitachi FT-NMR 60 MHz with TMS as the internal standard. GLC analyses were performed using SE-30 column (3 meters) with nitrogen as a carrier gas and FID detector on Shimadzu GC-9A model. High performance liquid chromatography (HPLC) analyses were done using ODS-18 (Zorbax, 150 mm×4.6 mm) column and methanol as eluent on Shimadzu LC-4A.

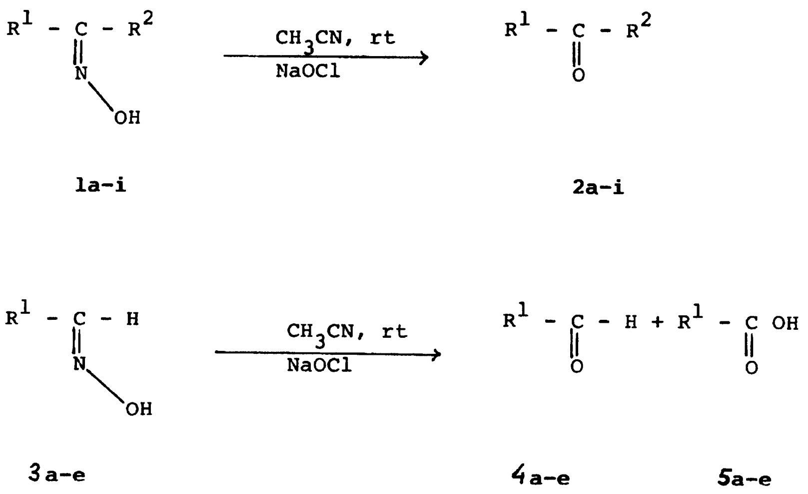
General Procedure. In a 100 ml conical flask, mounted over a magnetic stirrer, was placed a mixture of ketoximes or aldoxime (1 mmol) and $\mathrm{CH_3CN}$ (10 mL). Sodium hypochlorite solution (0.5 M) was added and the contents of the flask were stirred at ambient temperature. The reaction was monitored by TLC (eluent: petroleum ether/benzene). After disappearance of the starting material, the reaction was quenched with dil HCl, extracted with dichloromethane (10 mL×3) and washed with water (5 mL×2). The extract was dried over anhyd $\mathrm{MgSO_4}$ and filtered. The product (carbonyl compound) was obtained after removing the solvent on a rotary evaporator and drying in vacuo.

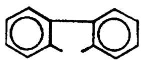
In case when a carboxylic acid was formed—as observed by TLC—the combined dichloromethane extract was treated with saturated solution of sodium bicarbonate (10 mL×2) to remove the acid. The dichloromethane layer was separated, dried (anhyd $\mathrm{MgSO_4}$) and concentrated on a rotary evaporator to obtain the carbonyl compound. The aqueous layer was acidified with dil HCl and extracted with dichloromethane (10 mL×3). After drying and concentrating as

Table 1. Deoximation of Ketoximes **1** with Sodium Hypochlorite

Run	Substrate, **1**	Time	Yield of **2**	Mp (°C)	
		min	%	Found	Reported
1	**a**	15	89	48	49[8)]
2	**b**	15	87	82	83[8)]
3	**c**	15	85	136	137[8)]
4	**d**	15	88	94	96[8)]
5	**e**	30	88	58	58[8)]
6	**f**	20	86	110	110—111[9)]
7	**g**	20	99[a)]	—	—
8	**h**	15	84	115	116[8)]
9	**i**	15	23.6[b,c)]	—	—
10	**i**	30	33[b,d)]	—	—
11	**i**	30	61[b,c)]	—	—
12	**i**	20	95[a,f)]	—	—

a) GLC yield confirmed by comparable retention time with authentic sample. b) Product was identified by superimposable IR spectra. c) Benzoic acid (60%) was also isolated. d) The molar ratio of substrate to NaOCl is 1 : 5; benzoic acid (48%) was also isolated. e) The molar ratio of substrate to NaOCl is 1 : 2; benzoic acid (23%) was also isolated. f) Reaction was carried out at pH 5—7 using 1 : 5 molar ratio of substrate to NaOCl.



1	R^1	R^2	**3**	R^1
a	Ph	Ph	**a**	Ph
b			**b**	3,4-(–OCH_2O–)C_6H_3
c	Ph	CH(OH)Ph	**c**	*p*-$CH_3OC_6H_4$
d	Ph	COPh	**d**	3,4-$(CH_3O)_2C_6H_3$
e	Ph	CH:CHPh	**e**	$CH_3(CH_2)_6$
f	PhCH:CH	CH:CHPh		
g	CH_3	CH_3		
h	–CH:CHCOCH:CH–			
i	Ph	CH_3		

Scheme 1.

above, the corresponding carboxylic acid was obtained.

The products were identified by mp, mixed mp, superimposable IR, and NMR spectra.

Procedure for Reactions at pH 5—7. In a 250 mL conical flask, mounted over a magnetic stirrer, is placed a mixture of ketoxime or aldoxime (1 mmol), CH_3CN (10 mL) and 50 mL of buffer solution (pH 4). Sodium hypochlorite (0.5 M) is added dropwise, in such a rate so as to maintain the pH value between 5—7. The reaction was monitored by TLC (eluent: petoroleum ether/benzene). After 20 min the reaction mixture is extracted with petroleum ether (bp 40—60 °C). The extract was dried over anhyd Na_2SO_4, filtered

Table 2. Deoximation of Aldoximes **3** with Sodium Hypochlorite[a]

Run	Substrate	Time	Molar ratio	Yield of product (%)		Mp (°C)	(R^1COOH)
	R^1CH_3=NOH	min	Oxime : NaOCl	(R^1CHO)[b,c]	(R^1CO_2H)[b]	Found	Reported
13	**a**	15	1 : 10	—	84	120	121[8]
14	**a**	15	1 : 5	12	80	120	121[8]
15	**a**	15	1 : 2.5	39	58	120	121[8]
16	**a**	15	1 : 5[d]	99[e]	—	—	—
17	**b**	30	1 : 10	65	15.5	210[f]	229[10]
18	**b**	15	1 : 5[g]	—	98	210[f]	229[10]
19	**c**	30	1 : 10	52	37	183	184[8]
20	**c**	15	1 : 5[d]	98[e]	—	—	—
21	**d**	30	1 : 10	57	36	179	180[8]
22	**e**	30	1 : 10	77[h]	16[h]	—	—

a) All reactions have been done with dropwise addition of 0.5 M NaOCl unless otherwise specified. b) Isolated yields unless otherwise stated. c) Product identified by NMR and superimposable IR spectra. d) Reaction done at pH 5—7. e) Yield determined by GLC; confirmed by comparable retention time with an authentic sample. f) The product sublimes at this temperature. g) Reaction done by one lot addition of the reagent unlike 'all' others, see a). h) Yield determined by HPLC; confirmed by comparable retention time with authentic sample.

and the solvent was removed in vacuo. The product mixture was analysed by GLC.

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