

## FERROUS ION INDUCED DECOMPOSITION OF ALKYL HYPOCHLORITES

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**Abstract**—The decomposition of primary, secondary and tertiary alkyl hypochlorites induced by ferrous and other one-electron oxidizable metal ions leads to  $\delta$ -chloro alcohols in yields of 34–76%. In decomposition of tertiary alkyl hypochlorites,  $\beta$ -fragmentation competes with intramolecular  $\delta$ -chlorination. Tertiary cycloalkyl hypochlorites containing five- or six-membered rings undergo  $\beta$ -cleavage giving the corresponding  $\omega$ -chloro ketones, while 1-methylcycloheptyl and 1-methylcyclooctyl hypochlorites by decomposition with ferrous ion proceed by transannular functionalization of  $\delta$ -carbon atom and  $\beta$ -cleavage as a competing reaction.

Alkyl hypochlorites containing a side chain of at least four carbons are readily converted to  $\delta$ -chloro alcohols on irradiation and this reaction has been developed into a successful method for  $\delta$ -chlorination of alcohols.<sup>1,2</sup> This type of reaction involving intramolecular hydrogen abstraction from  $\delta$ -carbon has been extensively investigated<sup>1-4</sup> and applied in the functionalisation of non-activated  $\delta$ -methyl groups.<sup>5-7</sup>

Since intramolecular chlorination has been also achieved either by irradiation<sup>8,9</sup> or by ferrous ion induced decomposition<sup>10</sup> of N-chloro amines we undertook to investigate decomposition of alkyl hypochlorites induced by metal ions.

This paper describes intramolecular chlorination of long chain primary, secondary and tertiary alkyl and cycloalkyl hypochlorites induced by ferrous ion and other one-electron oxidizable metal ions. We found that this reaction is more suitable for the preparation of  $\delta$ -chloro alcohols (and derived tetrahydrofuranes).

Initial experiments were carried out with *n*-hexyl hypochlorite 1 and crystalline ferrous sulfate was used as an inducing reagent. Decompositions were performed in the dark, in carbon tetrachloride solution at room temperature and under nitrogen. Under those conditions 4-chloro-1-hexanol was obtained in 76% yield in addition to 2-ethyltetrahydrofuran (6%), *n*-hexanal (3–5%) and hexanol (10%) (Table 1, Scheme 1).

In order to prevent intermolecular  $\alpha$ -hydrogen abstraction by chlorine radicals with formation of hydrogen chloride and subsequent decomposition of hypochlorite, reactions were performed in the presence of sodium bicarbonate (to neutralize hydrogen chloride) or dichloro ethylene (to trap chlorine radicals).<sup>1,4</sup>

Since in the ferrous ion induced decompositions of alkyl hypochlorites without light, the same reaction

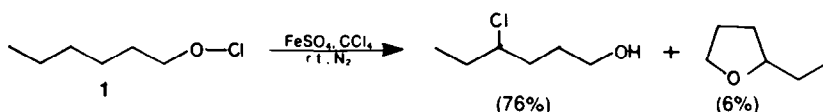
products and yields were obtained as found by Walling under irradiation conditions,<sup>1,4</sup> we carried out reactions in daylight in the presence of ferrous ions and similar yields of reaction products were obtained.

Although primary and secondary alkyl hypochlorites are unstable in daylight and at room temperature, the rate of decomposition in the dark without the ferrous ions and under described conditions is less than 5% during 2 hr. However, the decomposition of primary and secondary alkyl hypochlorites in the dark but induced with ferrous ion is almost complete (97%) during 1.5 hr. This evidence and the reaction products strongly indicate that the ferrous ion participates in the homolytic cleavage of O–Cl bond in alkyl hypochlorites (Scheme 2), i.e. ferrous ion is a convenient reagent for generation of alkoxy radicals from alkyl hypochlorites, as it has been widely used for decomposition of peroxy bond in alkyl hydroperoxides and other peroxy compounds.<sup>11-13</sup>

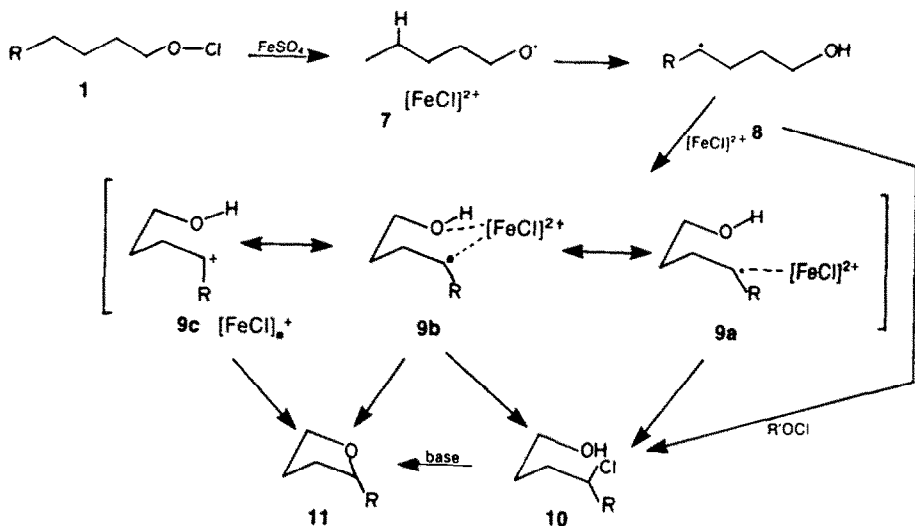


Decomposition by ferrous ion is extended to secondary and tertiary alkyl hypochlorites and results are summarized in Table 1. As can be seen, primary 1, and secondary 2–4 alkyl hypochlorites afforded satisfactory yields of the corresponding  $\delta$ -chloro alcohol, while decompositions of tertiary hypochlorites 5, 6 were accompanied with  $\beta$ -fragmentation as a competing reaction to the intramolecular hydrogen abstraction. Our results obtained in the ferrous ion induced decomposition of alkyl hypochlorites suggest that this method should be complementary to photolytically induced decomposition in the preparation of  $\delta$ -chloro alcohols.

We believe that the mechanism of this reaction involves homolysis of the O–Cl bond induced by the



Scheme 1.



ferrous ion thus forming an alkoxy radical 7 (Scheme 2). Reaction further proceeds with intramolecular hydrogen abstraction from  $\delta$ -carbon atom generating the corresponding  $\delta$ -carbon radical 8.<sup>1,14-17</sup> As it was found that  $\delta$ -functionalization is the most favoured reaction when a ratio of ferrous sulfate to alkyl hypochlorite of 0.5-1:1 was used, this suggests that this is not a simple chain reaction as was found in the irradiation reaction. By using a catalytical amount of ferrous sulfate considerable lower yields of  $\delta$ -chloro alcohols were obtained. We

assume that  $\delta$ -chlorination of radical 8 (Scheme 2) in the presence of the ferric ion, formed by the one-electron oxidation of the ferrous ion in the decomposition step, proceeds involving coordination of the  $\delta$ -hydroxyalkyl radical 8 with the ferric ion (structures 9a-9b, Scheme 2) and a subsequent oxidative ligand transfer process with formation of  $\delta$ -chloro alcohol 10,<sup>18,19</sup> although chain reaction, as described by Walling,<sup>1,4</sup> cannot be completely excluded.

Formation of cyclic ether 11 in the initial experiments

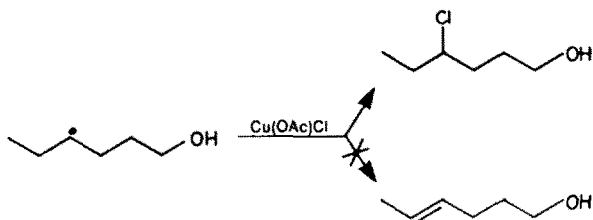


Table 1. Decomposition of alkyl hypochlorites by ferrous sulfate in the dark. Products and their yields (%)<sup>a</sup>

Alkyl hypochlorite	$\delta$ -Functionalization <sup>b)</sup>		$\alpha$ -Fragmentation	Carbonyl compounds <sup>d)</sup>
<u>n</u> -Hexyl (1)	(76%) <sup>d)</sup>	(6)	-	<u>n</u> -Hexanal (3-5)
2-Hexyl (2)	(71)	(8)	-	2-Hexanone (7)
2-Hepyl (3)	(68)	(7)	-	2-Heptanone (5)
4-Octyl (4)	(67)	(9)	-	4-Octanone (8)
2-Methyl-2-hexyl (5)	(48)	(9)	<u>n</u> -Butyl chloride (10) <sup>e)</sup> <u>n</u> -Octane (4)	
2-Methyl-2-octyl	(51)	(10)	<u>n</u> -Hexyl chloride (8) <sup>f)</sup> <u>n</u> -Dodecane (10)	

a) Molar ratio of reactants were used (see Experimental)

b) Almost same ratio of reaction products was obtained when reactions were carried out on daylight.

c) The corresponding alcohols were obtained in yields up to 8%.

d) Similar yields were obtained by using 0.5-1 : 1 molar ratio of ferrous sulfate to n-hexyl hypochlorite, and also by

e) replacing  $\text{NaHCO}_3$  with 1,2-dichloro ethylene does not make remarkable change in the reaction products and their yields.

f) As a product of  $\beta$ -cleavage 2-hexanone was also obtained in 9% yield.

2-Octanone was isolated in 11% yield.

was attributed to the cyclization of  $\delta$ -chloro alcohol **10** during glc analysis; however, we performed glc analysis on 60°, 80° and 100° and almost the same yields of tetrahydrofuran derivatives were obtained. Cyclic ethers **11** were also formed in experiments when dichloroethylene was used as a trapping reagent for chlorine radicals, instead of sodium bicarbonate, indicating that cyclization of  $\delta$ -chloro alcohols **10** to tetrahydrofurans **11** by sodium bicarbonate in carbontetrachloride solution does not occur. From these observations we propose that cyclic ethers, in ferrous ion induced decomposition of alkyl hypochlorite can be formed either by involving structure **9b** where hydroxylic oxygen coordinates with ferric ion and with subsequent oxidative ligand transfer process, or by oxidation of  $\delta$ -carbon radical **8** to the corresponding carbonium ion **9c** and with subsequent cyclization to cyclic ether ring **11**.

Cyclization of  $\delta$ -chloro alcohol to tetrahydrofuran derivatives by means of prolonged action of silver ions has been described by Mihailović<sup>20</sup> and Boido<sup>21</sup> and it should be possible to achieve cyclization of  $\delta$ -chloro alcohol **10** by ferric ion. However, treatment of  $\delta$ -chloro alcohol with ferric salts and by prolonged stirring of reaction mixture after decomposition of alkyl hypochlorite containing ferric salts does not increase the yields of cyclic ethers.

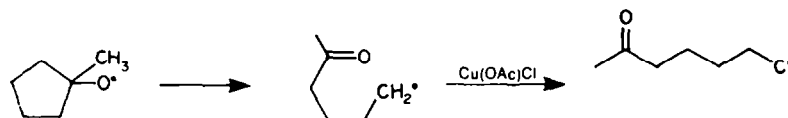
It was found that  $\delta$ -hydroxyalkyl radical of type **8** generated by ferrous ion induced decomposition of alkyl hydroperoxides<sup>12,13</sup> or dialkyl peroxides<sup>22</sup> and photolytically induced decomposition of alkyl nitrites<sup>23</sup> in the presence of cupric acetate, undergoes electron transfer oxidation affording  $\delta$ - (or  $\gamma$ -) unsaturated alcohols. However in the decomposition of alkyl hypochlorites

induced by ferrous ion in the presence of cupric acetate unsaturated alcohols were not obtained. Electron transfer oxidation of  $\delta$ -hydroxyl radical (such as **8**) to corresponding olefinic alcohols does not occur because cupric acetate and ferric salts (having chlorine as a ligand) undergoes a ligand exchange reaction giving  $\text{Cu}(\text{OAc})\text{Cl}$ . This mixed cupric salt rather serves as a ligand transfer reagent giving  $\delta$ -chloro alcohol than as an electron transfer reagent to form unsaturated alcohol (Scheme 3).

Decompositions of *n*-hexyl, 2-heptyl and 2-methyl-2-hexyl hypochlorite was carried out with several other one-electron oxidizable metal ions such as  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Cu}^+$  and  $\text{Tl}^+$ , and it was found in all experiments that intramolecular chlorination takes place. However, the yields of corresponding  $\delta$ -chloro alcohols and tetrahydrofurans were slightly to considerably lower than those obtained in the ferrous ion reactions. These results are summarized in Table 2. No correlation was found between ionisation potential, rate of decomposition and yields of products of intramolecular reaction or  $\beta$ -cleavage.

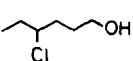





In decomposition of tertiary alkyl hypochlorites induced by ferrous and other metal ions,  $\beta$ -fragmentation reaction is somewhat more favoured (up to 25%) than photolytically induced reaction (13%),<sup>1,2</sup> increasing the  $\beta$ -cleavage process is probably due to the presence of metal ion in the formation step of alkoxy radical where transition state **12** can be postulated (Scheme 5).

By ferrous ion induced decomposition of tertiary cycloalkyl hypochlorites where intramolecular reaction is suppressed due to structural and conformational factors the  $\beta$ -fragmentation process becomes predominant. So in



Scheme 4.

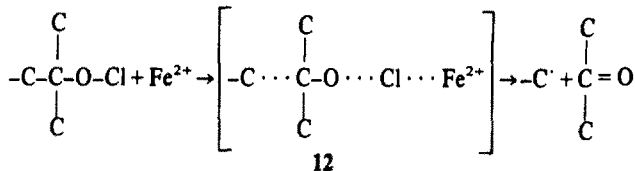
Table 2. Decomposition of alkyl hypochlorites by one-electron oxidizable metal ions in the dark. Products of  $\delta$ -functionalization and their yields (%)

Metal salts	Products of $\delta$ -functionalisation obtained from					
	<i>n</i> -Hexyl hypochlorite		2-Heptyl hypochlorite		2-Methyl-2-hexyl hypochlorite	
$\text{FeSO}_4$	 (76)	 (6)	 (71)	 (8)	 (48)	 (9)
$\text{NiCl}_2$	(56)	(0)	(68)	(8)	(42)	(12)
$\text{Co}(\text{OAc})_2$	(48)	(4)	(58)	(8)	(49)	(5)
$\text{CeCl}_3$	(59)	(6)	(51)	(0)	(43)	(2)
$\text{CuCl}$	(34)	(4)	(29)	(2)	(44)	(6)
$\text{Tl}_2\text{SO}_4$	(44)	(0)	(34)	(0)	(46)	(0)

a) Hexanal and hexanol were obtained in 1-2% and 10-55% yields, respectively

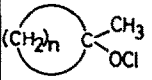

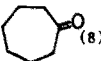
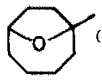
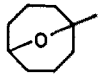
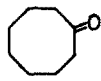
b) From the reaction mixture there were also isolated the corresponding ketone,  $\alpha$ -chloro ketone and alcohol in 5-35%, 5-7% and 10-33%, respectively.

c) In addition to products of  $\delta$ -functionalisation there were also obtained products of  $\beta$ -cleavage such as butyl chloride (8.12%), *n*-octane (2-5%) and 2-hexanone (4-9%).



Scheme 5.

Table 3. Decomposition of tertiary cycloalkyl hypochlorites by ferrous sulfate. Products and their yields (%)

	$\delta$ -Functionalization	$\beta$ -Fragmentation
$n = 4$ (13)	-	Cl-(CH <sub>2</sub> ) <sub>n</sub> COCH <sub>3</sub> (100)
$n = 5$ (14)	-	Cl-(CH <sub>2</sub> ) <sub>n</sub> COCH <sub>3</sub> (86)
$n = 6$ (15)	 (43)	Cl-(CH <sub>2</sub> ) <sub>n</sub> COCH <sub>3</sub> (10)  (8)
$n = 7$ (16)	 (20)  (27)	 (27)

the reaction of 1-methylcyclopentyl hypochlorite 13 with ferrous sulfate a quantitative yield of 6-chloro-2-hexanone was obtained (Table 3). Increasing the ring size up to 1-methylcyclooctyl hypochlorite 16  $\beta$ -fragmentation is decreased and transannular reaction, i.e. bicyclic ether formation is favoured. There are two possible ways in which  $\beta$ -cleavage may take place, the first involves ring opening with formation of  $\omega$ -chloro ketone and the second is alkyl group cleavage furnishing the corresponding cycloalkanone. The occurrence of  $\beta$ -fragmentation depends on the stability of the corresponding cyclic ketone. As can be seen from Table 3, 1-methylcyclopentyl 13 and 1-methylcyclohexyl hypochlorite 14 undergo only ring opening, while in the decomposition of 1-methylcycloheptyl hypochlorite 15 two competitive  $\beta$ -cleavage processes occur to an almost equal extent and 8-chloro-2-octanone and cycloheptanone were obtained in 10 and 8% yield, respectively. 1-Methylcyclooctyl hypochlorite 16 afforded only cyclooctanone as a fragmentation product which is in accordance with the greater stability of cyclooctanone than the cycloheptanone ring.

By comparing our results with photolytically induced decomposition of the same tertiary cycloalkyl hypochlorites<sup>24-26</sup> it can be seen that the fragmentation process is somewhat more involved in the ferrous ion decomposition of hypochlorite. So decomposition of tertiary cyclopentyl 13 and cyclohexyl hypochlorite 14 with ferrous sulfate should be a convenient method for preparation of the corresponding  $\omega$ -chloro ketones.

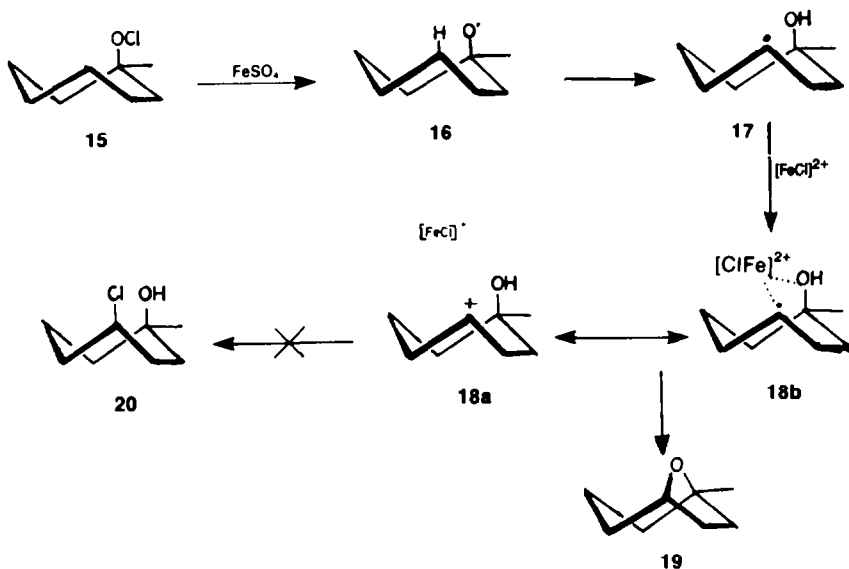
Decomposition of 1-methylcyclopentyl hypochlorite by ferrous sulfate was also performed in the presence of cupric acetate. However 5-hexen-2-one was not obtained and only 6-chloro-2-hexanone was isolated as a product of  $\beta$ -cleavage. The alkyl radical which arose from  $\beta$ -fragmentation of the alkoxy radical undergoes the ligand transfer with mixed cupric salt and no electron transfer process is involved.

Increasing the ring size increases the proximity factors for transannular hydrogen abstraction and formation of the corresponding bicyclic ethers. In the decomposition of 1-methylcycloheptyl hypochlorite 15 as a product of intramolecular reaction 1-methyl-1,4-epoxycycloheptane was formed and cycloheptanone and 8-chloro-2-octanone as products of  $\beta$ -cleavage were obtained, while 1-methylcyclooctyl hypochlorite gave a mixture of 1-methyl-1,4- (and 1,5-) epoxycyclooctane in addition to cyclooctanone (Table 3). In both reactions the corresponding chloro alcohols were not obtained. We believe that formation of bicyclic ether 19 does not involve the corresponding chloro alcohol 20 but cyclization proceeds involving alkoxy 16 and  $\delta$ -radical 17, either via corresponding carbonium ion 18 hydroxy formed by oxidation of carbon radical 17 with the ferric ion or by a ligand transfer process involving coordination of the ferric ion with the hydroxylic oxygen 18a in the  $\delta$ -hydroxyalkyl radical intermediate, as was suggested for formation of cyclic ethers from acyclic hypochlorite (Scheme 6).

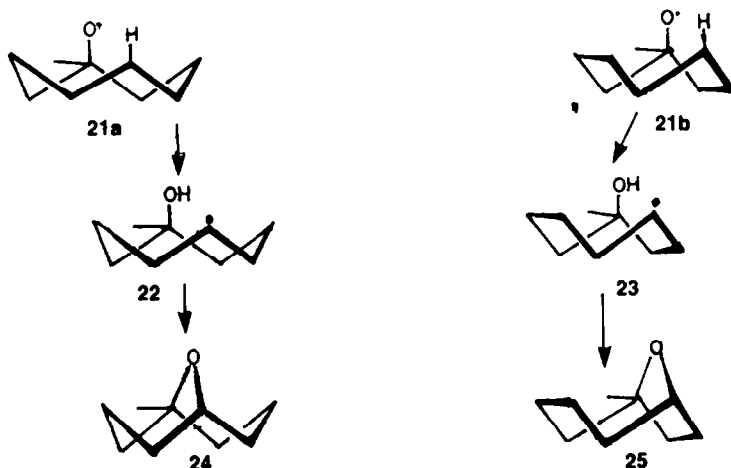
1-Methylcyclooctyloxy radical, generated by hypochlorite decomposition, undergoes 1,6-hydrogen transfer (with crown conformation of cyclooctane ring 21a) and transannular 1,5-hydrogen shift (from chair conformation 21b) thus generating carbon radicals 22 and 23, respectively. These radicals were subsequently oxidized to corresponding bicyclic ethers 24 and 25, respectively (Scheme 7). The mixture of these two bicyclic ethers was not separated, but on the bases of NMR and mass spectra we assumed that they were obtained in almost equal amount.

#### EXPERIMENT

Glc analysis and separations were performed on Varian 1400 and 90-P-3 instruments equipped with columns of XE-60 and OV-101 (on Chromosorb P (2m x 2mm, 2m x 6mm, respectively). IR spectra were recorded on Perkin-Elmer instrument Model 337 Grating (as film or CCl<sub>4</sub> soln). NMR spectra were recorded on



Scheme 6.



Scheme 7.

Varian A 60A instrument, using  $\text{CCl}_4$  as a solvent and TMS as internal standard. Mass spectra were performed on Varian-Atlas CH-4 spectrometer. All solvents in preparation and decompositions of hypochlorites were purified and checked by glc before use. Metal salts used in decompositions were p.a. purity grade.

#### Synthesis of alkyl hypochlorites

All primary, secondary and tertiary alkyl and cycloalkyl hypochlorites were prepared by the procedure of Walling and McGuinness<sup>27</sup> by reaction of appropriate alcohol (0.06 mole) in  $\text{CCl}_4$  (100 ml) with acetic acid (0.12 mole) and slurry of commercial calcium hypochlorite (containing 0.06 mole of active chlorine) in water (100 ml) at  $0^\circ$  in the dark. The organic layer was separated and dried over  $\text{CaCl}_2$ . Alkyl hypochlorites were used without isolation. Concentration of hypochlorites in  $\text{CCl}_4$  solns were determined iodometrically, and conversion of alcohols was quantitative since soln showed no  $-\text{OH}$  absorption in IR spectra, or extraneous NMR peaks. Solutions of tertiary hypochlorites could be stored in the refrigerator, in the dark for several days without considerable decomposition, while primary and secondary alkyl hypochlorites are less stable and were used immediately after preparation.

#### General procedure for decomposition of alkyl hypochlorites in the dark

To the carbon tetrachloride solution containing 0.06 mole of hypochlorite protected from the light, 0.03–0.06 mole of well powdered crystalline metal salts and 2 g of  $\text{NaHCO}_3$  were added and the reaction mixture was stirred under  $\text{N}_2$  at room temperature for 2–10 hr. Precipitated salts were filtered off and  $\text{CCl}_4$  solution was washed with water and dried over  $\text{CaSO}_4$ . Solvent was removed by distillation at atmospheric pressure and residue analysed by glc (up to  $60^\circ$ ). In some runs mixture was treated with KOH in methanol and cyclic ethers were isolated. The reaction products were identified by IR, NMR and mass spectra. Products and their yields are given in Tables 1–3.

#### Decomposition of n-hexyl hypochlorite

(a) *With ferrous sulfate (dark).* To the solution of n-hexyl hypochlorite (0.026 mole) in  $\text{CCl}_4$  (100 ml), 0.06 mole of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 2 g of  $\text{NaHCO}_3$  were added under  $\text{N}_2$ . The reaction flask was protected from the light and the reaction mixture stirred at room temperature overnight. From the reaction mixture were isolated 2-ethyltetrahydrofuran (6%), 4-chloro-n-hexanol (76%), hexanol (3–5%) and hexanol (up to 10%) and identified by IR, NMR and mass spectra. When 0.5–0.9:1 ratios

were used somewhat lower yields of  $\delta$ -functionalization products were obtained. Almost the same yields of 2-ethyltetrahydrofuran and 4-chloro-1-hexanol were obtained by running the reaction during daylight, as well as using dichloro ethylene instead of  $\text{CCl}_4$  and  $\text{NaHCO}_3$ .

(b) *With other metal ions (dark)*. Decomposition of n-hexyl hypochlorite was also carried out with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{Cu}_2\text{Cl}_2$  and  $\text{Ti}_2\text{SO}_4$ . The reactions were performed by using 0.03 mole of n-hexyl hypochlorite in 50 ml  $\text{CCl}_4$  and 0.03 mole of well powdered salts and 1 g of  $\text{NaHCO}_3$ . Products of decomposition and their yields are given in Table 2.

Decompositions of the other alkyl- and cycloalkyl hypochlorites by oxidizable metal ions were carried out under same experimental conditions. Products and their yields are summarized in Tables 1-3.

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