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THE OXIDATION OF ALCOHOLS AND ETHERS USING CALCIUM HYPOCHLORITE

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ABSTRACT

Calcium hypochlorite, a relatively stable, and easily stored and used solid hypochlorite oxidant, was found to oxidize secondary alcohols to ketones in excellent yields. Primary alcohols gave esters where both the acid and the alcohol portions of the ester were derived from the alcohol. Ethers were oxidized to esters though only in moderate yields.

While carrying out studies on the Grob-type cleavage of gamma-hydroxysulphones^{2,3} we attempted the preparation of the corresponding hypochlorite by the action of sodium hypochlorite on 2-tosylmethyl cyclohexanol⁴ Instead of the hypochlorite, an excellent yield of the corresponding ketone (2-tosylmethylcyclohexanone) was obtained. Subsequent to this conversion, we independently found that this method was general for converting secondary alcohols to ketones by the use of sodium hypochlorite or commercially available Chlorox solutions. Though our conditions differed somewhat, the results were essentially the same as those reported by Stevens⁵.

Table 1

Yield^a Yield Run Substrate Product Ref. NaOCI Ca(OCI)₂ /-Menthol 98% 98% 1 /-Menthone 9a,b Borneol 98% 99% 2 Camphor 9c 3 Norborneol Norcamphor 92% -10 4 Cyclohexanol Cyclohexanone 91% 98% 9c 2-tosylmethyl-2-tosylmethyl-5 98% 98% cyclohexanol⁴ cyclohexanone^C 3,5-dimethyl-3,5-dimethyl-6 93% 10 cyclohexanol cyclohexanone 7 5-cholesten-3-ol 4-cholesten-3-one 91% 91% 10^b 97% 9d 8 3-pentanol 3-pentanone 3-pentanol 87% 9d 9 3-pentanone

The Oxidation of Secondary Alcohols Using Ca and Na Hypochlorite

The instability of sodium hypochlorite solutions, however, led us to consider other hypochlorite reagents which would be more stable and handle. easier to Calcium hypochlorite⁶ is a commercially available solid and is inexpensive. Since this reagent does not decompose significantly when stored without light in a desiccator⁷, carrying out oxidations by weighing the required amount of solid oxidant represented a more convenient method than using solutions which would frequently have to be titrated. We now wish to report our results concerning the use of Calcium hypochlorite as an oxidant.

Oxidations of secondary alcohols with this reagent proceed smoothly, and in excellent yields at 0°C in a solvent containing acetic acid. Our results are given in **Table 1** for twelve compounds along with our

ni	ti alo re:	sodium	ny pocel horite. ⁸	80%	99%	9d
	11	diphenylcarbinol	benzolphenone	98%	-	9d
	12	2-tosylmethyl- 1-phenylethanol ⁴	a-tosylmethyl- acetophenone ^d	-	98%	-

- 1. Isolated yield.
- **2.** DCM was used instead of MeCN for solubility reasons.
- **3**. IR, DCM (cm⁻¹), 1710, 1320, 1150; NMR (CDCl₃) δ 7.1-7.9, (m, 4H), 3.8-4.02 (dd, 2H) 2.5 (s, 3H), 1.5-2.1 (m, 9H).
- **4.** mp: 130-131°C; IR, DCM (cm⁻¹) 1690, 1315, 1150; NMR (CDCl₃) δ 7.3-8.0 (m, 9H), 3.52 (s, 4H), 2.47 (s, 3H).

EXPERIMENTAL

A general procedure is outlined for the oxidation of I-menthol to I-menthone:

Thus, Menthol (3g, 19mmol) was dissolved in acetonitrile: acetic acid (3:2, 25ml) and added dropwise over a period of 10 minutes to a cooled (0°C) and stirred solution of calcium hypochlorite (1.84g, 12.7mmol) in water (40ml). Stirring was continued for 1 hr after which water (40ml) was added. The solution was extracted with DCM (4x30ml) and the organic layers washed with 10% sodium bicarbonate followed by an aqueous wash. After drying with Magnesium sulfate and evaporation of solvent, the crude product was distilled affording menthone (2.89g, 98%). The spectra (IR and NMR) were identical with those of authentic material.9,10

Oxidation of primary alcohols under identical conditions gave an aldehyde only in the case of benzyl alcohol¹¹. Other

primary alcohols gave esters as in Table **2**. This table also includes our results on the oxidation of ethers to esters. Though the yields were not nearly as good for the alcohols, the data is reported because of the unusual and potentially useful transformation¹². The ethers were oxidized under similar conditions as the alcohols except that the reactions were carried out at RT for 4-16 hours. Heating does not seem to increase yield.

We are presently carrying out studies to improve the yields on the ether to ester transformation and to utilize the primary alcohol oxidation for the preparation of lactones from a, ω -diols.

Table 2 Oxidation of Primary Alcohols and Ethers Using Calcium and Sodium Hypochlorite.

Run	Substrate	Product	Yield ^a Ca(OCI) ₂	Yield NaOCl	Ref.
1	Benzyl alcohol	benzaldehyde	98%	98%	10
2	1-pentanol	pentyl pentanoate	83%	91%	10
3	1-hexanol	hexyl hexanoate	98%	98%	9e
4	3-methylbutanol	3-methylbutyl isovalerate	76%	87%	10
5	ethyl alcohol	ethyl acetate		b	9b,10
6	ethyl ether	ethyl acetate	b		
7	butyl ether	butyl butanoate	40%		10
8	THF	γ-butyrolactone	68%		9b,10
9	Tetrahydropyran	δ-valerolactone	56% ^C		9b,10

- **1**. Isolated Yield
- **2.** Yield not calculated due to the volatility of the products

The Oxidation of Alcohols and Ethers Using Calcium Hypochlorite - [ww... http://www.erowid.org/archive/rhodium/chemistry/ether2ester.hypochlori...

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