Tetrahedron Letters,Vol.23,No.1,pp 35-38,1982
Printed in Great Britain
0040-4039/82/010035-04$03.00/0

THE OXIDATION OF ALCOHOLS AND ETHERS USING CALCIUM HYPOCHLORITE [$Ca(OCl)_2$]

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Summary: 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 yield.

While carrying out studies on the Grob-type cleavage of γ-hydroxy sulphones[2,3] we attempted the preparation of the corresponding hypochlorite by the action of sodium hypochlorite on 2-tosylmethyl cyclohexanol[4]. Instead of the hypochlorite, an excellent yield of the corresponding ketone (2-tosylmethyl cyclohexanone) 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 recently reported by Stevens[5].

The instability of sodium hypochlorite solutions however led us to consider other hypochlorite reagents which would be more stable and easier to handle. Calcium hypochlorite[6] is a commercially available solid and is inexpensive. Since this reagent does not decompose significantly when stored without light in a desiccator[7], 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 $Ca(OCl)_2$ as an oxidant.

Oxidations of secondary alcohols with calcium hypochlorite proceeds smoothly, and in excellent yield at 0° in a solvent containing acetic acid. Our results are given in Table 1 for twelve compounds along with our initial

Table 1. The Oxidation of 2°-Alcohols Using Calcium and Sodium Hypochlorite.

Run	Substrate	Product	% Yield[a]		Reference
			Ca(OCl)$_2$	NaOCl	
1	ℓ-menthol	ℓ-menthone	98	98	9a,b
2	borneol	camphor	98	99	9c
3	norborneol	norcamphor	92	--	10
4	cyclohexanol	cyclohexanone	91	98	9c
5	2-tosylmethyl-cyclohexanol[4]	2-tosylmethyl-cyclohexanone[c]	98	98	--
6	3,5-dimethyl-cyclohexanol	3,5-dimethyl-cyclohexanone	93	--	10
7	5-cholesten-3-ol	4-cholesten-3-one	91	91	10[b]
8	3-pentanol	3-pentanone	97	--	9d
9	3-pentanol	3-pentanone	--	87	9d
10	2-octanol	2-octanone	80	99	9d
11	diphenylcarbinol	benzophenone	98	--	9d
12	2-tosylmethyl-1-phenyl ethanol[4]	α-tosylmethyl acetophenone[d]	--	98	--

a) Isolated yield

b) Methylene chloride was used as solvent instead of acetonitrile for solubility reasons.

c) Ir, CH_2Cl_2 (cm^{-1}) 1710, 1320, 1150; nmr, $CDCl_3$(δ), 7.1-7.9 (m, 4H), 3.8-4.02 (dd, 2H) 2.5 (s, 3H), 1.5-2.1 (m, 9H); ms, m/e 266, 111.

d) Mp 130-131°; ir, CH_2Cl_2 (cm^{-1}) 1690, 1315, 1150; nmr, $CDCl_3$ (δ) 7.3-8 (m, 9H), 3.52 (s, 4H), 2.47 (s, 3H); ms, m/e 288; Analysis Calc. for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.45; O, 16.66; s, 11.11. Found C, 66.52; H, 5.49; S, 11.18.

results using sodium hypochlorite[8]. A general procedure is outlined for the oxidation of ℓ-menthol to ℓ-menthone. Thus ℓ-menthol (3 g, 19 m mol) was dissolved in acetonitrile: acetic acid (3:2 25 ml) and added dropwise over a period of ten minutes to a cooled (0°C) and stirred solution of $Ca(OCl)_2$ (1.84 g, 12.7 m mole) in water (40 ml). Stirring was continued for 1 hr after which water (40 ml) was added. The solution was extracted with CH_2Cl_2 (4 x 30 ml) and the organic layers washed with 10% $NaHCO_3$ followed by an aqueous

Table 2. Oxidation of 1° Alcohols and Ethers Using Calcium and Sodium Hypochlorite.

Run	Substrate	Product	% Yield[a]		Reference
			$Ca(OCl)_2$	NaOCl	
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-methyl butanol	3-methyl butyl 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	tetrahydrofuran	γ-butyrolactone	68	--	9b,10
9	tetrahydropyran	δ-valerolactone	56[c]	--	9b,10

a) Isolated yield

b) Yield not calculated due to the volatility of the products but significant conversion was indicated by ir and nmr analysis.

c) Yield obtained by gc analysis.

wash. After drying with $MgSO_4$ and evaporating the CH_2Cl_2 the crude product was distilled affording ℓ-menthone (2.89 g, 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 alcohol[11]. Other primary alcohols gave esters as tabulated in Table 2. This table also includes our results on the oxidation of ethers to esters. Though the yields were not nearly as good as for the alcohols, the data is reported because of the unusual and potentially useful transformation[12]. The ethers were oxidized under similar conditions as the alcohols except that the reactions were carried out at room temperature for from 4-16 hrs. Heating does not seem to increase the yield.

We are presently carrying out studies to improve the yields on the ether to ester transformation and to utilize the 1° alcohol oxidation for the preparation of lactones from α-ω diols.

cknowledgement: We thank the NSF (CHE 7910245) and NIH (Biomedical Research upport Grant RR 07044) for support of this work.

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(Received in USA 12 October 1981)