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NOVEL METHOD OF DEOXIDATION OF ALCOHOLS AND ITS USE IN SYNTHESIS OF COVALENT PERCHLORATES

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Summary : Alcohols can be effectively deoxidated by treatment with chlorine and sulfur in the presence of pyridine with incorporation of an external nucleophile from added salts.

Since 1978 we have studied systematically the intriguing phenomenon of competitive reactivity of nucleofugic anions,such as ClO_4^-, FSO_3^-, TfO^-, TsO^- etc.,in the reactions which proceed via carbocationic-like intermediate or transition state with developed carbocationic character [1]. We have shown that these anions,which have been considered to be "super-weak" or "feeble" nucleophiles (or even "non-nucleophiles") exhibit rather powerful nucleophilic reactivity in competition with "normal" nucleophiles (Hal^-, AcO^- etc.). This phenomenon has been observed for electrophilic additions [1a,b],acid catalysed epoxyde ring openig [1b],deamination of amines [1b],oxidative deiodination of alkyl iodides [1b,c],chlorinolysis of sulfides [1d]. This phenomenon has extensive synthetic [1a-d] and theoretical ramifications [1b,e]. In this paper we describe (i) novel reaction of deoxidation of alcohols, and (ii) the competitive binding of ClO_4^- anions to give covalent perchlorates in the course of this reaction.

The replacement of oxygenated moieties with various functional groups is of considerable importance in synthetic endeavours. The poor nucleofugic ability of the hydroxyl function almost entirely excluded pathway involving direct S_N2 substitution. The most useful methods include either the transformation of OH group into derivatives possessing much better leaving groups [2] or transient activation (protonation, complexation with Lewis acids,dichloricarbene [3] etc.) and over the years,many approaches have been developed for that purpose [3b].

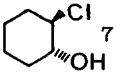
In the search for a mild procedure for the direct deoxidation of alcohols we have finally found that hydroxyl moiety can be effectively displaced by the treatment with Cl_2+S in the presence of pyridine and inorganic salts which play role of a source of an external nucleophile. The net result of the reaction can be expressed by eq. 1 :

$$\text{(1)} \quad R\text{-}OH + Cl_2 + S + Z^+X^- + Py \longrightarrow R\text{-}X + Z^+Cl^- + SOCl_2 + Py\cdot HCl$$

where X = OTs, OTf or $OClO_3$; Z = Li or $n\text{-}Bu_4N$

The reactions are performed in Et_2O or AcOEt at 25-30°C in the presence of pyridine [4]. Reaction products and yields are summarized in the Table. The reaction of $n\text{-}C_8H_{17}OH$ without an added salt proceeds smoothly to give the corresponding chloride,$n\text{-}C_8H_{17}Cl$, with high yield. However,the most interesting results were obtained in the presence of the salts containing weak nucleophilic (TsO^-) or even super-weak nucleophilic (ClO_4^- and TfO^-) anions. These anions can successfully compete with Cl^- in the final step of the reaction.The reaction of **7** proceeds nonstereospecifically to give both cis (2) and trans (3) perchlorates,first one being predominant. This is a rare example of the formation of cis-product in substitution reaction of trans-2-chlorocyclohexyl derivatives [5].The formation of **3** from cyclohexanol is due to elimination process with subsequent chloroperchloration of the transient

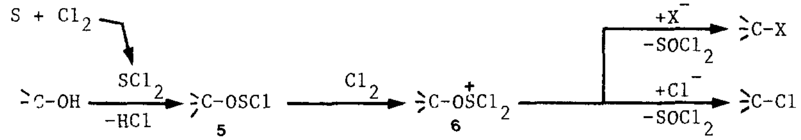
Table. Deoxidation of alcohols by Cl_2+S in the presence of added salts.

No	Alcohol	Salt(mol-eqv)	Product (yield,%)[a]
1	n-octanol	none	n-octylchloride,**1** (68)
2	n-octanol	$n\text{-}Bu_4N^+TsO^-$ (1)	n-octyltosylate (15), **1** (60)
3	n-octanol	$LiOSO_2CF_3$ (2)	n-octyltriflate (25), **1** (40)
4	n-octanol	$LiClO_4$ (5)	n-octylperchlorate (41), **1** (28)
5	 7	$LiClO_4$ (5)	cis-2-chlorocyclohexyl perchlorate,**2** (42) trans-2-chlorocyclohexyl perchlorate,**3** (11) 1,2-dichlorocyclohexane,**4** (10)
6	cyclohexanol	$LiClO_4$ (5)	**2** (15), **3** (43), **4** (10)

[a] Yields refer to the isolated,chromatographically and spectroscopically homogeneous materials.

olefin (cf.Ref 1a).Analogous pathway has been observed for oxidative deiodination of iodocyclohexane in methanol [6] and in the presence of salts of perchloric acid [1c].

The mechanistic scheme of this reaction seems to include the formation of chlorosulfenate **5**,chlorination of which gives chlorosulfonium ion **6**, bearing very good nucleofugic group $-OS^+Cl_2$ [7],which, in turn,is capable to undergo nucleophilic substitution even by a such feeble nucleophile as perchlorate anion (eq 2).

(2) 

Thus, we have found the convenient method of deoxidation of alcohols which can be used to obtain either chlorides or covalent derivatives of nucleofugic anions such as triflates and perchlorates.

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4. Excess of chlorine was passed during 5-10 min into the stirred mixture of 2 mmol of alcohol,10 mmol of powdered sulfur and 2 mmol of pyridine in 20 ml of AcOEt. The workup included a filtration,washing with water,drying, evaporation in vacuo and chromatography on silica gel. All esters of perchloric and sulfonic acids have been preparatively isolated and identified by comparison (IR,NMR) with previously obtained samples (refs 1a,b).The reaction in the absence of pyridine also gives the corresponding deoxidation products but the reaction mixture contains much more components.
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7. (a)Analogous mechanism via intermediacy of chlorosulfonium salt of type **6** has been suggested for chlorinolysis of alkyl arylsylfenates in AcOH (Ref 7b). We have shown that this reaction in the presence of lithium perchlorate gives covalent perchlorates. For instance, trans-2-chlorocyclohexyl 2,4-dinitrophenylsulfenate reacts with chlorine in AcOEt in the presence of 5 mol-eqv of lithium perchlorate to give 2-chlorocyclohexyl perchlorates **2** (40% yield) and **3** (27% yield). (b)J.G.Traynham and A.W.Foster,J.Am.Chem.Soc.,**1971**,93,6216 (see also E.N.Givens and H.Kwart,Ibid.,**1968**,90,386).

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