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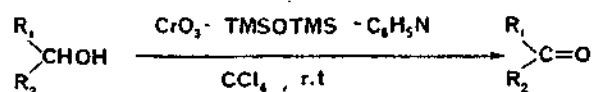
Oxidation of Alcohols by Chromic Anhydride-Hexamethyldisiloxane-Pridine

Jong Gun Lee*, Dong Soo Ha, and Hee Jong Lim

Department of Chemistry, Pusan National University, Pusan 609-735. Received July 22, 1988

One of the most important application of chromium (VI) compounds is the oxidation of alcohols to the carbonyl compounds^{1,2}. Chromium salts and complexes of heteroaromatic bases seem to be preferable to the conventional reagents in aqueous acids^{3,5}. Excellent procedures utilizing neutral chromium(VI) compounds such as chromyl chloride⁶ and di-*t*-butyl chromate(DTBC)⁷ are also available.

The insertion of chromic anhydride into silicon-oxygen bonds of siloxanes to form silyl chromates has been known for a long time⁸. However, the useful application of these silyl chromates in organic reactions are scarce. Bis(triphenylsilyl) chromate was reported as an initiator for the polymerization of olefins⁹ and as an oxidizing agent for hydroxyalkyl ferrocenes¹⁰. Chromic anhydride is known to be easily inserted to produce bis(trimethylsilyl) chromate¹¹. We now report that this reagent in the presence of pyridine is mild and efficient for the oxidation of alcohols to carbonyl compounds. The procedure is very simple and convenient.



Chromic anhydride was stirred with hexamethyldisiloxane in carbon tetrachloride. It was readily dissolved to form a red nearly homogeneous solution. Pyridine (0.1 mol) was added followed by an alcohol to be oxidized in a minimum amount of carbon tetrachloride. After 4 hour of stirring, the reaction mixture was filtered through a short column of silica gel. Carbonyl compounds of high purity can usually be obtained by simply evaporating off the low boiling solvents and by-products.

All primary alcohol tested were oxidized to aldehydes and secondary alcohols to ketones. Allylic alcohols were oxidized without carbon-carbon double bond cleavage. The role of pyridine remains unclear. In the absence of it, however, the oxidation is very sluggish yielding aldehyde in less than 30% yield. The reaction conditions and the yield of the carbonyl compounds are listed in Table 1.

Table 1. Oxidation of Alcohols with BTSC-Pridine^a

Substrate	Time (hr)	Product	% Yield ^b
1-hexanol	4	1-hexanal	80.0
1-Octanol	4	1-octanal	84.6
2-hexanol	4	2-hexanone	87.5
cyclohexanol	4	cyclohexanone	81.6
menthol	4	menthone	81.6
borneol	4	camphor	77.9
cinnamyl alcohol	2	cinnamaldehyde	91.0
benzyl alcohol	2.5	benzaldehyde	85.0
p-methoxybenzyl alcohol	2	p-anisaldehyde	88.5
geraniol	3	geranial	67.3 ^c
2-methyl-3-buten-2-ol	2 ^d	3-methyl-2-butenal	72.5
2-phenyl-3-buten-2-ol	1.5 ^d	3-phenyl-2-butenal	18.0 ^e
1-vinylcyclopentanol	1.5 ^d	α,β -unsaturated aldehyde	43.0
1-methyl-2-cyclohexen-1-ol	1.5 ^d	3-methyl-2-cyclohexenone	84.0

^a2 equivalents of BTSC and pyridine were used. ^bisolated yield. ^cstarting alcohol was not recovered. ^dReaction at -10 °C. ^eAcetophenone was the major product (72%).

The oxidizing properties of BTSC closely resemble those of di-*t*-butyl chromate(DTBC). When prepared in an anhydrous form from the reaction of chromyl chloride and *t*-butyl alcohol in the presence of pyridine, DTBC can oxidize alcohols to carbonyl compounds in very high yields⁷.

Chromic anhydride-hexamethyldisiloxane-pyridine system has definite advantages over anhydrous DTBC. The reagent system can be easily prepared from the cheap off the shelf chemicals. The reaction conditions are very mild. The workup procedure is simple. The yield is higher or comparable to those using the other popular chromium(VI) oxidizing agents.

Some tertiary allylic alcohols were oxidized to produce α,β -unsaturated carbonyl compounds. 2-Methyl-3-buten-2-ol,



for example, can be oxidized to 3-methyl-2-butenal in 72% yield, when treated with BTSC. Since the vinyl addition to ketones yields the tertiary alcohols, this sequence provides a way to synthesize the α,β -unsaturated carbonyl compounds with two carbon elongation from ketones. Phenyl substituted enones or enals produced by this procedure underwent carbon-carbon double oxidation, and alkanophenone was obtained as a major final product.

We are currently studying other features of this interesting reagent.

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Effect of EDTA on the Formation and Stability of CdS Colloidal Semiconductor

Joon Woo Park*, Kyung Ran Min, and Eun Yong Jeung

Department of Chemistry, Ewha Womans University, Seoul 120-750, Received July 29, 1988

Colloidal CdS semiconductor particle has much of the desired characteristics for using it in solar energy conversion systems and photocatalytic reactions.^{1,2} The semiconductor particle is usually prepared *in situ* from cadmium salt solution by addition of sulfide solution or by exposure to H₂S gas. The properties of the particle are greatly dependent on the size of the particle,³ which varies with preparation mode. In CdS-mediated photochemical reduction reaction, e.g. water splitting, the photogenerated electron of the semiconductor is transferred to oxidant. For sustained reaction, the presence of sacrificial electron donor which supplies electrons to the positive holes of the semiconductor particles is required. Ethylenediaminetetraacetate (EDTA) is frequently utilized for the purpose.^{4,7} However, EDTA forms complex CdEDTA²⁻ with Cd²⁺. Thus the presence of EDTA in solution is expected to affect the formation and behavior of CdS colloid. Present communication reports results of investigations on this aspect.

Colloidal CdS was prepared by mixing 1.0×10^{-3} M CdCl₂ solution with 1.5×10^{-3} M Na₂S solution at equal volume ratio. Both solutions contained desired concentration of Na₂EDTA ($0-3.0 \times 10^{-3}$ M) and pH of the solutions was adjusted to 8.0 ± 0.3 with HCl/NaOH. Formation of CdS colloid was detected by yellow coloration visually and followed by absorption spectra. The spectra were taken after vigorous vortex of the mixtures aged for desired period. Figures 1a-c show absorption spectra of the mixtures after 10 min, 24 hrs and 48 hrs of mixing. The most remarkable effect of EDTA was retardation of CdS colloid formation. In the absence of EDTA, the mixture showed yellow color instantaneously.

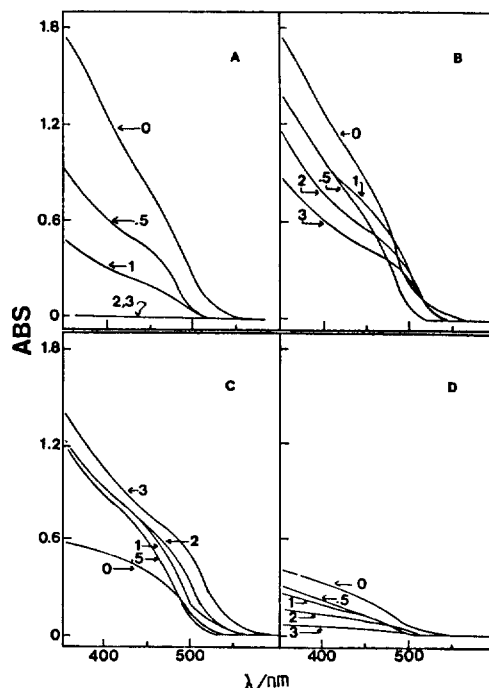


Figure 1. Absorption spectra of solutions after mixing 1.0×10^{-3} M CdCl₂ and 1.5×10^{-3} M Na₂S solutions in equal volume ratio in the presence of EDTA at pH 8: A, after 10 min; B, after 24 hrs; C, after 48 hrs. Solutions for spectra D included 6×10^{-4} M Tris and other conditions were the same as C. The concentrations of EDTA in mM unit are shown in Figures.