Tetrahedron Letters No. 50, pp 4597-4600. 1976. Pergamon Press. Printed in Great Britain.

OXIDATION USING DISTANNOXANE I. SELECTIVE OXIDATION OF ALCOHOLS

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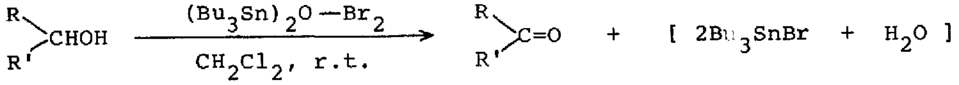
(Received in Japan 25 September 1976; received in UK for publication 26 October 1976)

Recent two publications concerning the oxidation of alcohols to carbonyl compounds via *stannoxane* (1)-*bromine*[1] and -N-bromosuccinimide (NBS)[2] prompt us to report our new results on the direct and selective oxidation of alcohols by distannoxane (2)-bromine system.

$$\underset{}{ROH \longrightarrow \underset{(1)}{R'_3Sn\text{-}OR}} \qquad\qquad \underset{(2)}{(R_3Sn)_2O}$$

Although during our investigation, Mukaiyama et al.[3] reported the direct oxidation of alcohols (benzylic, allylic, and secondary alcohols) by distannoxane (2)-Br_2, we have found the distannoxane-Br_2 oxidation was highly selective. Thus, secondary or benzylic alcohols were oxidized to the corresponding carbonyl compounds, whereas normal primary alcohols gave a trace of or no aldehydes. This behavior has provided a novel selective oxidation method towards polyhydroxy compounds.

At first, we examined the oxidation of various kind of alcohols using hexabutyldistannoxane (HBD). The experimental procedure was similar to that employed for the dihydroxy compounds described later.



$$\begin{matrix}R\\R'\end{matrix}\!\!>\!CHOH \xrightarrow[CH_2Cl_2,\ r.t.]{(Bu_3Sn)_2O-Br_2} \begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}O \;+\; [\ 2Bu_3SnBr \;+\; H_2O\ ]$$

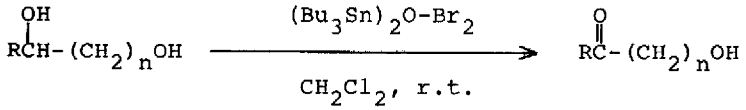
The results obtained here are listed in TABLE I.

TABLE I. Oxidation of Alcohols[4]

Alcohols	Product	Yield(%)[a]
$PhCH_2OH$	PhCHO	85[b]
$C_6H_{11}OH$	cyclohexanone	91[b]
Cinnamyl alcohol	Cinnamaldehyde	48[b]
n-Butanol	n-Butyraldehyde	0
3-Phenyl-1-propanol	3-Phenylpropionaldehyde	∼0
Geraniol	Geranial	0
syn-Diphenylethylene glycol	Benzoin	63[c]

[a] The yields have not been optimized in any case. [b] as 2,4-dinitrophenylhydrazone. [c] isolated yield.

As shown in TABLE I, the results indicate clearly that primary alcohols are inert towards the present method. So we, next, investigated the selectivity for dihydroxy compounds which are composed of primary and secondary hydroxy groups.



$$\mathrm{R\overset{OH}{C}H\text{-}(CH_2)_nOH} \xrightarrow[\mathrm{CH_2Cl_2,\ r.t.}]{\mathrm{(Bu_3Sn)_2O\text{-}Br_2}} \mathrm{R\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_nOH}$$

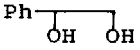
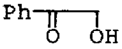
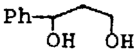
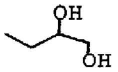
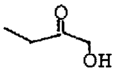
In all cases, the ir spectrum of the crude reaction mixture exhibited only one carbonyl absorption attributable to ketone group but not aldehyde, and each product isolated was confirmed as ω-hydroxyketone.

The following procedure is representative. To a solution of styreneglycol (0.57g, 4 mmol) and hexabutyldistannoxane (HBD) (2.7 ml, 5.2 mmol) in dry methylene chloride (15 ml), bromine (0.27 ml, 5.2 mmol) solution in methylene chloride (5 ml) was added dropwise at room temperature with stirring under argon atomosphere. The mixture was stirred for 1∼3 hr at room temperature. Evaporation of the solvent and standing the oily residue overnight gave crystalline hydroxyacetophenone. 0.41g (76%) $\nu_{C=O}$ 1686 cm^{-1}, mp 84-6°C(n-hexane) (Lit[5], mp 86°C).

In the case of 1,3-dihydroxybutane, 4-hydroxy-2-butanone was isolated by distillation, (66%), bp 73-74°C/13 mmHg (Lit.[6] bp 73-76°C/12 mmHg), nmr (neat); δ2.2 (s,3H,CH_3) 2.67 (t,2H,$COCH_2$), 3.8 (t,2H,CH_2O), 4.3 (s,1H,OH).

The results are summarized in TABLE II.

TABLE II. Selective Oxidation of Dihydroxy Compounds[4]

Dihydroxy compounds	Product	Yield(%)[a]
		76
		86[b]
		66
		68

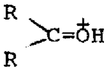
[a] isolated yield. [b] as 2,4-dinitrophenylhydrazone.

The present method has potential utility due to the following aspects; (1) availability of HBD, (2) mild and almost instant completion of the reaction, (3) high selectivity which provides a facile synthetic method for the preparation for ω-hydroxyketones, (4) neutral conditions in which the dehydration, especially from ω-hydroxyketones is prevented.

Detailed mechanisms for the above oxidation are not clear at present time. However, instant disappearance of the color of bromine when bromine was added to a solution of HBD indicates the fast reaction of bromine with HBD, presumably to give species such as (3).[7]

$$\mathrm{HBD} + \mathrm{Br_2} \longrightarrow \underset{(3)}{\mathrm{Bu_3SnOBr}} + \mathrm{Bu_3SnBr}$$

The species (3) may oxidize alcohols to the corresponding carbonyl compounds via ionic or radical process. Although radical process cannot be entirely excluded, above high selectivity and especially, exclusive formation of benzoin instead of benzil from syn-diphenylethyleneglycol even in the presence of two equimolar amount of HBD-Br_2 suggest the involvement of the ionic species such as oxonium ion (4) at a final stage.



$$R_2C{=}\overset{+}{O}H \quad (4)$$

In summary, distannoxane-bromine oxidation seems to be very promising and the studies on the other possible applications of the method are now in progress.

References

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3. K. Saigo, A. Morikawa, and T. Mukaiyama, Bull. Chem. Soc. Japan, 49, 1656 (1976).
4. All compounds obtained here had satisfactory physical and spectral data.
5. Z. Rappoport, "Handbook of tables for Organic Compound Identification" third edition, The chemical Rubber Co., Cleveland, Ohio, 1967, p. 89.
6. J.T. Hays, G.F. Hager, H.M. Engelman, H.M. Spurlin, J. Amer. Chem. Soc., 73, 5369 (1951).
7. One support for the involvement of the positive bromine species such as (3) seemed to be derived on the reaction of HBD-Br_2 with sulphide. As expected, we have observed that thioanisol was oxidized to methyl phenyl sulphoxide on treatment with HBD-Br_2. The details of the sulphide oxidation using HBD-Br_2 or -NBS systems will be reported in near future.