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A NEW METHOD FOR THE OXIDATION OF ALCOHOL TO CARBONYL COMPOUND

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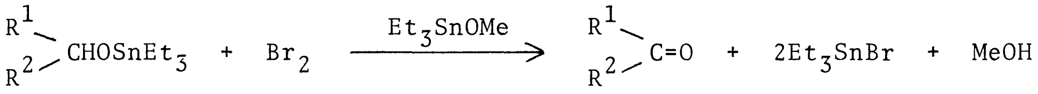
It was found that various triethyltin alkoxides, prepared easily from alcohols and triethyltin methoxide, are oxidized by bromine to give the corresponding carbonyl compounds in good yields.

We report here a highly selective and operationally convenient method for the oxidation of a wide variety of alcohols to the corresponding aldehydes or ketones. It is expected that this method will find widespread use among currently available procedures[1-7] for the oxidation of alcohol.

The oxidation of triethyltin alkoxide with bromine in the presence of triethyltin methoxide affords the corresponding aldehyde or ketone in good yield as shown in the following equation.



$$\begin{matrix}R^1\\R^2\end{matrix}\!>\mathrm{CHOSnEt_3} + \mathrm{Br_2} \xrightarrow{\mathrm{Et_3SnOMe}} \begin{matrix}R^1\\R^2\end{matrix}\!>\mathrm{C{=}O} + 2\mathrm{Et_3SnBr} + \mathrm{MeOH}$$

The following experimental procedure is illustrative; a solution of geraniol (3.08 g, 20 mmol) and triethyltin methoxide (5.69 g, 24 mmol) in toluene (40 ml) was refluxed for 8 hr and methanol was azeotropically removed. After removal of the solvent, triethyltin salt of geraniol was obtained in 92% yield (6.63 g) by distillation. To a solution of the triethyltin salt of geraniol (679 mg, 1.89 mmol) and triethyltin methoxide (754 mg, 3.18 mmol) in THF (20 ml), a solution of bromine (310 mg, 1.94 mmol) in THF (10 ml) was added dropwise within 15 min at room temperature under an argon atmosphere. As soon as the addition of bromine solution was over, the reaction mixture was quenched with 5% $Na_2S_2O_3$ solution (5 ml) and 5% KOH solution (20 ml). The resulting mixture was extracted with ether (60 ml) and the ethereal layer was washed with 5%KOH solution (20 ml) and with brine. After evaporation of the solvent, geranial (269 mg, 94%), identified by nmr spectrum and vapor phase chromatographic analysis, was isolated by preparative thin layer chromatography. It is noted that the oxidation of geraniol affords geranial in high yield and by-products such as geranic acid (further oxidized product), neral (stereoisomer of geranial) and addition products of bromine to the olefinic linkages could not be detected by vapor phase chromatography.

Similarly, the triethyltin salt of alcohols, such as cinnamyl alcohol, (E)-hex-2-en-1-ol, piperonyl alcohol, benzyl alcohol, α-phenylethanol, and octan-2-ol were successfully oxidized to the corresponding carbonyl compounds in good yields as summarized in the table.

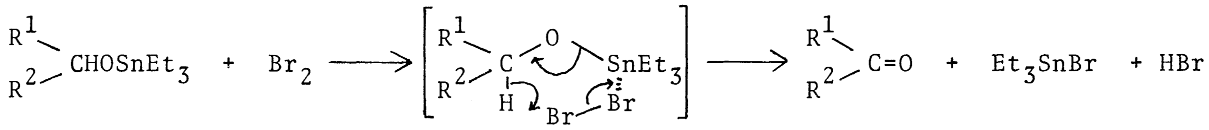
Table

Alcohol	triethyltin alkoxide yield (%)	solvent	oxidation product	yield(%)
Geraniol	92	THF	Geranial	94[a)]
Cinnamyl alcohol	84	THF	Cinnamaldehyde	92[b)]
(E)-Hex-2-en-1-ol	78	THF	(E)-Hex-2-enal	71[b)]
Piperonyl alcohol	86	THF	Piperonal	96[a)]
Benzyl alcohol	78	THF	Benzaldehyde	81[b)]
α-Phenylethanol	78	THF	Acetophenone	78[b)]
		CH_2Cl_2		70[b)]
		C_6H_6		66[b)]
Octan-2-ol	86	THF	Octan-2-one	85[b)]

a) isolated yield b) yield by vapor phase chromatography with 2m, 10% Carbowax 20M column.

The effect of the solvent on the yields of acetophenone examined by the oxidation of triethyltin α-phenylethoxide in THF, dichloromethane or benzene indicates that THF is a suitable solvent for this oxidation (see Table).

The oxidation of triethyltin alkoxide (I) with bromine (II) would proceed through a six-membered cyclic intermediate (III) to form carbonyl compound (IV), triethyltin bromide (V) and hydrogen bromide (VI). Hydrogen bromide (VI) produced is readily scavenged by triethyltin methoxide (VII) resulting in the formation of inert compounds as triethyltin bromide (V) and methanol (VIII).



(I) (II) (III) (IV) (V) (VI)

$$\underset{\text{(VI)}}{HBr} + \underset{\text{(VII)}}{Et_3SnOMe} \longrightarrow \underset{\text{(V)}}{Et_3SnBr} + \underset{\text{(VIII)}}{MeOH}$$

Further works on the scope and utility of the reactions are now in progress.

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