# Selective Oxidation of Alcohols and Oxidative Lactonization of Diols with Trichloromelamine

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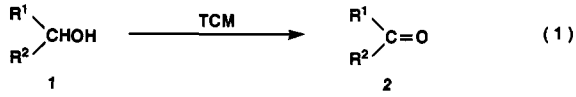
Trichloromelamine (TCM) can be viewed as a positive halogen compound, because the 1,3,5-triazine ring possess strong electron-withdrawing character. However, there are few papers concerning the utilization of TCM in organic synthesis.[1,2] We report here a simple and selective oxidation of alcohols to the corresponding carbonyl compounds and oxidative lactonization of diols with TCM under mild conditions.

When cyclohexanol was allowed to react with TCM with stirring in methylene chloride at room temperature for 3 h, cyclohexanone was obtained in 90% yield. The yield



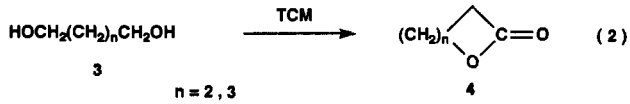

1 2 (1)

was not affected by adding benzoquinone or hydroquinone as radical scavengers. On the other hand, under the same conditions, *N*-chlorosuccinimide, a typical positive *N*-halo compound afforded α-chlorocyclohexanone in 43% yield.

As shown in Table I, the oxidation of a primary alcohol, 1-octanol, occurred slowly to afford octanal accompanied by some byproducts. With benzyl alcohol, the oxidation product, benzaldehyde, was obtained quantitatively at a moderate rate. For the oxidation of substituted benzyl alcohols, the yield of benzaldehydes after 20 h was reduced markedly by the introduction of electron-withdrawing groups. Secondary alcohols such as cyclohexanol, 2-octanol, and α-phenylethyl alcohol were oxidized rapidly to the corresponding ketones in high yields. But, the oxidation of benzhydrol and benzoin required a long time for completion of the reaction, indicating the importance of steric effects.

Since the possibility of selective oxidation was indicated by the results described above, the oxidation of diols containing primary and secondary hydroxy groups was examined. When styrene glycol was treated with TCM, α-hydroxyacetophenone was obtained exclusively. This result demonstrates that oxidation with TCM occurs on a secondary hydroxy group preferentially (Table II).

Furthermore, oxidation of 1,4-butanediol (3) with TCM in methylene chloride afforded an unexpected product, γ-butyrolactone (4), in 87% yield (Table II).




3 (n = 2, 3) 4 (2)

**Table I. Oxidation of Alcohols with TCM[a]**

| entry | alcohol (1) | time (h) | product (2) | yield (%) |
|---|---|---|---|---|
| 1 | 1-octanol | 20 | octanal | 56 |
| 2 | 2-octanol | 4 | 2-octanone | 92 |
| 3 | cyclohexanol | 3 | cyclohexanone | 90 |
| 4 | benzyl alcohol | 20 | benzaldehyde | 83 |
| 5 | *p*-chlorobenzyl alcohol | 20 | *p*-chlorobenzaldehyde | 65 |
| 6 | *p*-bromobenzyl alcohol | 20 | *p*-bromobenzaldehyde | 64 |
| 7 | α-phenylethyl alcohol | 1 | acetophenone | 98 |
| 8 | benzhydrol | 90 | benzophenone | 99 |
| 9 | benzoin | 125 | benzil | 98 |

[a] Reaction conditions: [TCM]/[alcohol] = 1. In $CH_2Cl_2$ at room temperature.

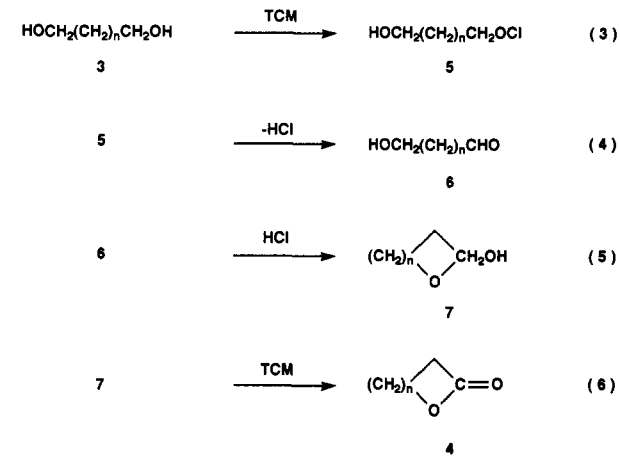
**Table II. Oxidation of Diols with TCM[a]**

| entry | alcohol | solvent | time (h) | product | yield (%) |
|---|---|---|---|---|---|
| 1 | styrene glycol | $CH_2Cl_2$ | 15 | α-hydroxyacetophenone | 92 |
| 2 | 1,4-butanediol | $CH_2Cl_2$ | 12 | γ-butyrolactone | 87 |
| 3 | | $CHCl_3$ | 12 | | 74 |
| 4 | | $CH_3CN$ | 12 | | 68 |
| 5 | | pyridine | 12 | | 0[b] |
| 6 | 1,5-pentanediol | $CH_2Cl_2$ | 12 | δ-valerolactone | 95 |

[a] Reaction conditions: [TCM]/[diol] = 2. [b] Most of 1,4-butanediol was recovered.

This reaction also proceeded in chloroform and acetonitrile, but pyridine was not a suitable solvent. δ-Valerophenone was also obtained from the corresponding diol, 1,5-pentanediol. Lactones of four- or seven-membered rings were not produced from the corresponding diols.

From the above results, the following mechanism which involves the oxidation of a hemiacetal might be proposed. Firstly the reaction of 3 with TCM would give oxidation product of one of the hydroxyl groups, ω-hydroxy aldehyde 6 through the hypochlorite 5, and followed by cyclization to afford the hemiacetal 7. The hemiacetal 7 would be further oxidized to the lactone 4. A similar mechanism has been proposed for the ruthenium-catalyzed lactonization of diols.[3]




Some methods have been reported for the oxidative lactonization of diols by using reagents such as silver carbonate on Celite,[4] ruthenium complexes[3,5-7] palladium

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complexes,[8] rhodium complexes,[9] bromine with nickel benzoate,[10] sodium bromite,[11] oxoaminium salts,[12] hydrogen peroxide with heteropoly acids,[13] and quaternary ammonium polyhalides.[14] Compared with these, the present method is useful because of the simple procedure, mild conditions, high selectivity, and low cost.

## Experimental Section

GLC (Carbowax 20 M, 10%, 2 m, and Silicone SE-30, 10%, 1 m) was used for separations and yield determinations. Trichloromelamine (TCM) was commercially available and used as received. Starting alcohols were purified by distillation or recrystallization.

**General Procedure for Oxidation of Alcohols with TCM.** To a solution of 50 mg (0.5 mmol) of cyclohexanol in 2.5 mL of methylene chloride was added 115 mg (0.5 mmol) of TCM. The reaction mixture was stirred vigorously at room temperature for 3 h. The solid was filtered and the organic layer was analyzed by GLC. Other alcohols were oxidized by the same method.

**Selective Oxidation of Styrene Glycol.** To a solution of 690 mg (5 mmol) of styrenediol in 25 mL of methylene chloride was added 2.30 g (10 mmol) of TCM. The reaction mixture was stirred for 15 h at room temperature. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography (Wakogel C-200, eluent: mixture of hexane and acetone (3:1)) to give a white solid (633 mg). The physical and spectral data of the product agreed with of those of an authentic sample of $\alpha$-hydroxyacetophenone.

**Oxidative Lactonization of 1,4-Butanediol.** To a mixture of 900 mg (10 mmol) of 1,4-butanediol and 50 mL of methylene chloride was added 4.59 g (20 mmol) of TCM. The mixture was stirred for 12 h at room temperature. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography (Wakogel C-200 eluent: methylene chloride) to give an oil (749 mg). The spectral data of the product agreed with those of an authentic sample of $\gamma$-butyrolactone.

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