# **PTC Oxidation of Alcohols using Hypochlorite**

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Oxidation is a ubiquitous reaction in organic chemistry and as such we felt it was necessary to include it in our laboratory curriculum. Among oxidants, nitric acid is dangerous, and salts of manganese or chromium are environmentally harmful and often messy; therefore, we sought other oxidizing agents devoid of these drawbacks and commercial bleach seemed appropriate.

In 1985 Mohrig et al. (1) published in this Journal a seminal paper on the use of household bleach in the oxidation of alcohols and the described procedure was then taken up by various laboratory textbooks (2). More recently, in this Journal Straub (3) published an oxidation procedure using TEMPO and bromide ion with commercial bleach to obtain benzil from benzoin. Moreover, alcohols and amines have been oxidized by bleach alone using phase transfer catalysis (4); this technique is now widely used in the laboratory (4) and could be included in the oxidation procedure as a demonstration of its usefulness. Therefore, we propose a procedure for the oxidation of benzhydrol to benzophenone, using bleach as the oxidant, ethyl acetate as the organic phase, and tetrabutylammonium hydrogen sulfate as the PTC catalyst. The oxidation is essentially complete in 30 min, and the yields range from 70% to 85% after recrystallization (eq 1).

## $R_2OH + CIO^- -> R_2CO + CI^- + H_2O$

The whole preparation can be done in a half-day laboratory period. It also should be noted that ethyl acetate is less toxic and cheaper than dichloromethane used in (3) and (4). In our hands dichloromethane gave poor yields with long oxidation times.

The substrate also can be an alicyclic alcohol; using nearly the same procedure as with benzhydrol, cycloheptanol can be oxidized to cycloheptanone with a yield of 76%. The ketone is pure by gas chromatography, which is especially interesting because the very close boiling points of both products (185°C for cycloheptanol and 179 °C for cycloheptanone) would make separation of a mixture quite difficult.

As Straub rightly points out, bleach does not keep well. It is essential that fresh bleach be used, otherwise yields and purity are low.

#### **Experimental Procedure**

Caution: Bleach is an inhalation and contact irritant and is dispensed under the hood. Benzhydrol and tetrabutylammonium hydrogen sulfate are irritants.

Benzhydrol and tetrabutylammonium hydrogen sulfate were purchased from Janssen Chimica and used as received. Ethyl acetate was distilled before use.

In a 250-mL Erlenmeyer flask 50 mL (100 mmol) of commercial bleach solution are added to 3.68 g (20 mmol) of benzhydrol and 0.35 g (1 mmol) of tetrabutylammonium hydrogen sulfate in 50 mL of ethyl acetate. The flask is stoppered and vigorously stirred (magnetic bar) for 30 min.

The organic phase is decanted, washed with 25 mL of saturated brine (twice) and 15 mL of water (twice), dried on magnesium sulfate, filtered and evaporated. Crude benzophenone is obtained as a syrup that crystallizes rapidly. It can be recrystallized from hexane. Yield: 2.52-3.05 g (69-84%); mp 47-48°C.

#### **Oxidation of Cycloheptanol**

The experimental set-up was the same as above with only a change in the concentrations. We used 4.56 g of cycloheptanol (40 mmol), 0.72 g of tetrabutylammonium hydrogen sulfate (2 mmol) in 50 mL of ethyl acetate and 100 mL of bleach. Stirring time was 1 h, and the work-up was the same as above, ending with careful evaporation of ethyl acetate on the rotary evaporator. The yield is 3.42 g (76%) of slightly yellowish liquid, pure by gas chromatography and with the same retention time as that of authentic cycloheptanone. (Carbowax 20M on Chromosorb-HMDS, 120°C).

## Literature Cited

- 1. Mohrig, J. R.; Nienhuis, D. M.; Linck, C. F; Van Zoeren, C.; Fox, B. G.; Mahaffy, P.G. J. Chem. Educ. 1985, 62, 519-521.
- (a) Fieser, L. F.; Williamson, K L. Organic Experiments, 7th ed. D.C. Heath: Lexington, MA, 1992, pp 265-266; (b) Roberts, R. M.; Gilbert, J. C.; Martin, S. F. Experimental Organic Chemistry; Saunders: Orlando, FL, 1994, pp 485-486.
- 3. Straub, T S. J Chem. Educ. 1991, 68, 1048-1049.

- 4. Lee, G. A.; Freedman, H. H. Tetrahedron Lett. 1976, 1641-1644.
- 5. (a) McIntosh, J. M. J. Chem. Educ. 1978, 55, 235-238; (b) Gokel, G. W; Weber, W P. J. Chem. Educ. 1978, 55, 350-354; (c) Gokel, G. W; Weber, W E J. Chem. Educ. 1978, 55, 42933.