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 curriculum. Among oxidants, nitric acid is dangerous, and salts of manganese or chromium are environmentall and often messy; therefore, we sought other oxidizing agents devoid of these drawbacks and commercial blea appropriate.

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

$$R_2OH + ClO^- \rightarrow R_2CO + Cl^- + H_2O$$

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

The substrate also can be an alicyclic alcohol; using nearly the same procedure as with benzhydrol, cyclohepta oxidized to cycloheptanone with a yield of 76%. The ketone is pure by gas chromatography, which is especiall because the very close boiling points of both products (185°C for cycloheptanol and 179 °C for cycloheptanone 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 yiel 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 rece 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 benzhydrol and 0.35 g (1 mmol) of tetrabutylammonium hydrogen sulfate in 50 mL of ethyl acetate. The flask 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), drie magnesium sulfate, filtered and evaporated. Crude benzophenone is obtained as a syrup that crystallizes rapid 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 of bleach. Stirring time was 1 h, and the work-up was the same as above, ending with careful evaporation of e on the rotary evaporator. The yield is 3.42 g (76%) of slightly yellowish liquid, pure by gas chromatography ar same retention time as that of authentic cycloheptanone. (Carbowax 20M on Chromosorb-HMDS, 120°C).

Literature Cited

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