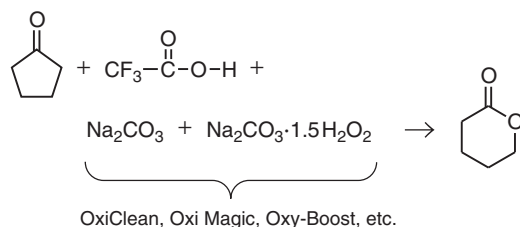


# The Baeyer–Villiger Oxidation with Trifluoroacetic Acid and Household Sodium Percarbonate

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The Baeyer–Villiger oxidation is a widely used reaction for converting ketones to esters (1). The oxidizing agent that is generally used for the reaction is commercially available *m*-chloroperoxybenzoic acid (MCPBA), and because this contains about 20% *m*-chlorobenzoic acid, it is safe to both store and use. The pure reagent, however, is known to be shock sensitive, and this perhaps helps explain the scarcity of Baeyer–Villiger experiments in one- or two-semester introductory organic lab courses. It has, at the very least, prompted some researchers to look for alternative reagents for carrying out the Baeyer–Villiger reaction in their research laboratories (2). One of these, peroxytrifluoroacetic acid, can be generated in situ from sodium percarbonate and either trifluoroacetic acid (TFA) (3) or trifluoroacetic anhydride (TFAA) (4). We report here the use of household sodium percarbonate and TFA to conveniently carry out a Baeyer–Villiger oxidation in a large-section introductory organic chemistry laboratory course:



In the past few years sodium percarbonate has become a popular laundry aid (5). This is especially true in Europe because it avoids the environmentally unfriendly boron of sodium perborate and chlorine of sodium hypochlorite (6). In the United States the success of OxiClean has led to the introduction of several brands of percarbonate-based laundry products such as Oxy-Boost and Clorox Oxi Magic.

## Procedure and Results

TFA, 3.0 mL, is added to 0.150 mL cyclopentanone in a round-bottom flask. A balloon containing 0.50 g household sodium percarbonate is secured over the opening of the flask and then manipulated so that the sodium percarbonate runs from the balloon into the flask. The reaction mixture (with the balloon still attached so that there is no contact with TFA vapors) is allowed to react at ambient temperature for 15 minutes with occasional swirling. A workup with cold water and methylene chloride is carried out in a fume hood. Evaporation of the solvent gives about a 50% yield of  $\delta$ -valerolactone.  $^1\text{H}$  NMR analysis allows the students to easily see that the desired transformation has taken place and that impurities are minimal. When reported yields are much higher than 50%, it is usually due to the presence of trifluoroacetic acid or methylene chloride, and these are easily seen in the  $^1\text{H}$  NMR spectrum.

We use this experiment with sections ranging up to 27 students. Each student works individually and records his or

her own NMR spectrum. The experiment is easily completed in a 3-hour lab period.

Similar results were obtained when students in two lab sections converted cyclohexanone to  $\epsilon$ -caprolactone by this procedure. Although the procedure has not been student tested, we have also converted benzophenone to reasonably pure phenyl benzoate. This procedure led to a 66% yield when we heated the sample in an 80 °C water bath for 10–15 minutes. Further purification of the phenyl benzoate was achieved by recrystallization from 95% ethanol (mp 65–66 °C; lit. 70 °C).

## Hazards

Household sodium carbonate–sodium percarbonate is irritating to the eyes, respiratory system, and skin. TFA can cause chemical burns to the skin, and it poses an inhalation hazard. Methylene chloride and chloroform-*d* are both toxic, irritating to the eyes and skin, and may cause cancer. Eye protection and rubber gloves must be worn throughout this experiment. The dispensing of TFA, the workup, and the preparation of the NMR sample should be carried out in a fume hood.

It should be noted that, in general, peroxyacids can constitute a decomposition hazard. Because of this and because of the corrosive nature of TFA, scale-up is not advised.

## Discussion

A disadvantage of this experiment is that TFA must be present in more than just a stoichiometric quantity; in fact, it is used as the solvent. Although this increases both the cost and safety risk, both of these are minimized by the scale of the experiment. We attempted to cut down on the quantity of TFA even further by diluting it with various quantities of acetic acid, but the results were unsatisfactory. Kang and Jeong (4) have reported the use of sodium percarbonate with small quantities of TFAA in methylene chloride to carry out the Baeyer–Villiger oxidation, but we found that the rigorously anhydrous conditions that were required made the procedure unsuitable for our purposes.

A search of *Chemical Abstracts* shows that three different compounds have the name “sodium percarbonate”. These are listed in Table 1. Sodium carbonate hydrogen peroxide adduct

Table 1. Sodium Percarbonate Listings in the *Chemical Abstracts*

Formula	CAS Number
$\text{Na}^+ \text{ } ^-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}^- \text{ } \text{Na}^+$	4452-58-8
$\text{Na}^+ \text{ } ^-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \text{ } \text{Na}^+$	3313-92-6
$\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$	15630-89-4

(the third entry in Table 1) is the one that is used in household laundry products. A sample of 100%  $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$  would contain 32.5%  $\text{H}_2\text{O}_2$  or 15.3% “available oxygen”. However, we are not aware of any commercial source of 100% sodium percarbonate; it is always sold as a mixture of sodium percarbonate and sodium carbonate. Even reagent grade sodium percarbonate from Sigma–Aldrich contains enough sodium carbonate to bring the quantity of  $\text{H}_2\text{O}_2$  down to ~25%. To examine the viability of various brands of household sodium percarbonate for this experiment, we determined their  $\text{H}_2\text{O}_2$  composition using standard iodometric and permanganometric methods (7). We found that the  $\text{H}_2\text{O}_2$  content varies from about 11% to 25%. Some of these brands also contain additives that can cause emulsions in the workup or show up in the NMR of the Baeyer–Villiger product. Although some widely available brands work just fine (see the online supplement), we consider Oxy-Boost to be the best choice for this experiment. It has a high  $\text{H}_2\text{O}_2$  composition and no undesirable additives, but it is currently available only on the Internet (8). Our second choice is one of the OxiClean products (OxiClean Baby Stain Soaker) and it is available in any grocery or discount store.

We feel that the novelty, brevity, and ease of carrying out this experiment will make it a valuable addition to the menu of experiments available to teachers of one- or two-semester introductory organic chemistry courses, and it will complement other Baeyer–Villiger experiments. One recent report in this *Journal* describes the use of MCPBA in a solventless Baeyer–Villiger reaction (9). Another involves the use of genetically engineered *Escherichia coli* to carry out the reaction (10). Two other Baeyer–Villiger experiments are geared for more advanced students (11, 12).

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$^1\text{H}$  NMR spectra

A table showing the suitability of ten different household sodium percarbonate products