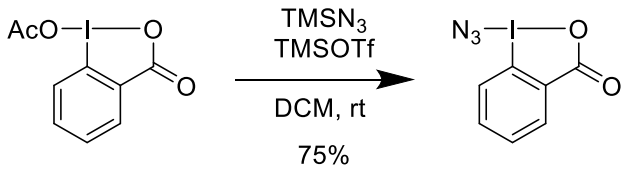
Report of the accident on July 10, 2017 using azidobenziodoxolone at LCSO

Before the accident: two detonations on small scale (20-30 mg) were observed when adding the compound to a flask containing an organocatalyst and a substrate (both solids). The compound is shock sensitive as demonstrated by hammer test.

Accident report

Used experimental protocol



Caution: reaction carried out behind a safety shield! Following a reported procedure, the starting material (1.00 g, 3.28 mmol, 1.00 equiv, synthesized in our laboratory) was stirred in dry DCM (3 mL, dried by passage over activated alumina under nitrogen atmosphere) in a thoroughly washed round-bottom glass flask, then $TMSN_3$ (0.66 mL, 4.9 mmol, 1.5 equiv, 94% from Alfa Aesar, catalogue number L00173-22) was cautiously added. A catalytic amount of TMSOTf (3 µL, 0.02 mmol, 0.005 equiv, Fluorochem, catalogue number S20400-250g) was added last to the mixture which was then stirred for 30 minutes. The solvent was then removed under reduced pressure at room temperature and the residue was dried in vacuo for one hour to give a yellow solid, which was washed with pentane (2x10 mL), cold acetone (2x5 mL) and pentane (2x 10 mL) and dried one hour in high vacuo. For each wash, the following procedure was followed: add solvent, stir 5 min, filtered on a frit, breaking larger pieces with metal spatula, and remove solvent during one minute on the frit. Usual yield around 70% (not determined on this batch due to the accident, see below).

Note: this is the reported method 2 in EROS:

http://onlinelibrary.wiley.com/doi/10.1002/047084289X.rn02053/abstract?selectedXmlId=rn02053-eo-c00022&userIsAuthenticated=false&deniedAccessCustomisedMessage=

With the difference of smaller reaction scale and the solvent used for washing (hexane was used in EROS). Acetone was found to be more efficient for removing yellow impurity in the compound.

Accident:

On the day of the experiment, the researcher (experienced postdoc having done already 200 experiments with the compound without any accident) wanted to use the batch immediately after preparing it to have the best quality possible. In the previous experiments, he had just filled the flask with nitrogen and stored the compound in the fridge for several weeks. This time, after drying 1 h in vacuum, he filled the flask with air and remove it from the vacuum line to weight it on the balance. The compound was first scratched from the wall of the flask with the spatula and then he slightly shook the flask (with the spatula in) to collect the solid at the bottom. At this point, it detonated. The flask was pulverized. As it was open, most of the energy went fortunately upwards.

Consequences:

The left hand had multiple blooding small cuts and burns (1. Degree and 2. Degree on the thumb). Minor cuts also on the face and between face and chest (areas not protected by the lab coat). The safety glasses protected the eyes. Hearing was imparted through the detonation.

Immediate treatment at the emergency room of the local hospital followed. It was decided not to remove the glass fragments, as they were very small and should be resorbed naturally. If not the case, an operation may be needed later. Hearing problems, high noise sensitivity and headaches slowly decreased over two weeks. Work incapacity for two weeks. At this point, no long-term damage expected.

Analysis:

The cause of explosion could not be identified. Ongoing hypotheses:

- Remaining impurities: HN_3? (but the wash was very thorough and careful)
- Explosive impurities formed with acetone (but intensive wash afterwards and no volatile should be left).
- Initiating non-volatile impurities, such as traces of metal
- The compound was pure, but the explosion was initiated by shock (very small one!) or electrostatic charging (via friction? indeed method of work not optimal in this case)

Proposed measures:

- Whenever possible, avoid using this compound!
- Diminish batch quantities (< 500 mg starting material)
- All actions behind safety shield (including weighting) with enhanced protection (explosion resistant mask and gloves)
- Action against electrostatic and shock (in particular no metal spatula, possibly avoid glass?)
- Diminish explosion potential of reagent by structure or formulation modification.

It seems very difficult to identify surely the cause(s) of explosion, exactly the same steps having been done several times in the lab, therefore the way to go is probably to envisage chemical modifications by adding stabilizing additive or changing the structure of the reagent (diminish nitrogen to carbon ratio) to decrease its explosion potential.