# **Purification of Ketones by Sodium Bisulfite**

## by Eleusis

So you've got this slop in a beaker that may or may not have that tasty little carbonyl compound that'll end up making some amine We Know And Love, but you've experienced disappointment in the past when trying to vacuum distill it. Maybe it's that hand vacuum pump you splurged for out of the Edmund Scientific catalog, or maybe you should try forming the bisulfite addition product instead.

It is a somewhat well known fact that sodium bisulfite will add to the carbonyl group of a ketone to form a crystalline addition product. If the parent ketone is of large enough molecular weight, the product will be insoluble in water. The parent ketone can then be recovered at a later time by decomposition with sodium hydroxide. This is a doubly good trick in that it gives us an excellent way to get pure ketone from an impure reaction matrix and it also allows the long term storage of an otherwise unstable ketone prior to its use.

Now, this doesn't \*eliminate\* the need for a proper (vacuum) distillation of the ketone, but it does make such a process much more pleasant in that when recovering from the bisulfite, there will be little tar and/or polymerized crap to deal with. This means greatly reduced cleaning for those precious flasks, and, possibly, higher yields. The bisulfite addition is a fairly general process, and may be adapted to many different ketones (keeping the molar ratios in proportion), however, there are going to be some ketones which will either not react or react to a low extent (mainly ones in which there is significant steric hindrance to the carbonyl carbon). In cases where the carbonyl carbon is on an aliphatic side chain to some other funky ring structure, there is little steric hindrance, and so the reaction proceeds quickly and nearly quantitatively. Finally, there is the limitation that that ketone (or ketone containing slop) be reasonably free of acidic or basic impurities, as these will interfere with the formation of the addition product.

### 1) Preparation of the bisulfite reagent

(This must be prepared just prior to use, as it will autooxidize within hours if left to it's own devices.)

Add 52g sodium bisulfite (NaHSO3, .5moles) to approximately 90mL of distilled water at room temperature with vigorous stirring (slightly more water may be used to get it all into solution). Add a volume of denatured alcohol of about 70% of the solution's volume (ie - if you end up with 100mL of solution, add 70mL of alcohol) then add more water to just dissolve the precipitate (~60mL).

### 2) Reacting with the ketone

Slowly drip .25moles of ketone(\*) into a beaker containing the bisulfite solution with vigorous magnetic stirring. The 2:1 molar ratio insures that all of the ketone will be converted. Let sit on the stirrer for an additional 30-45 minutes then filter on a vacuum Buchner funnel. Wash the crystals with 20-50mL of denatured alcohol. Dry in a vacuum dessicator or open tray then store in a stoppered glass bottle until needed.

(\*) If adding an impure reaction matrix, add as much solution as you expect to contain .25moles of ketone.

### 3) Recovering the ketone

Add the ~.25moles of bisulfite addition product to a separatory funnel then slowly pour in 105mL of 10% Sodium Hydroxide solution (w/w). Separate out the aqueous layer (which may be on top or on bottom depending on the ketone), saturate with salt (NaCl), and extract with 50mL of ether (toluene or benzene ok if the ketone is of high enough bp). Combine the extract with the ketone layer and strip off the ketone by distillation (condense and reuse!). Distill the ketone residue, preferably under vacuum (if you're making what I think you're making), to yield up to 90%, depending on the purity of the starting ketone, of course.

Refs to chase: A. Vogel, "Practical Organic Chemistry"

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