



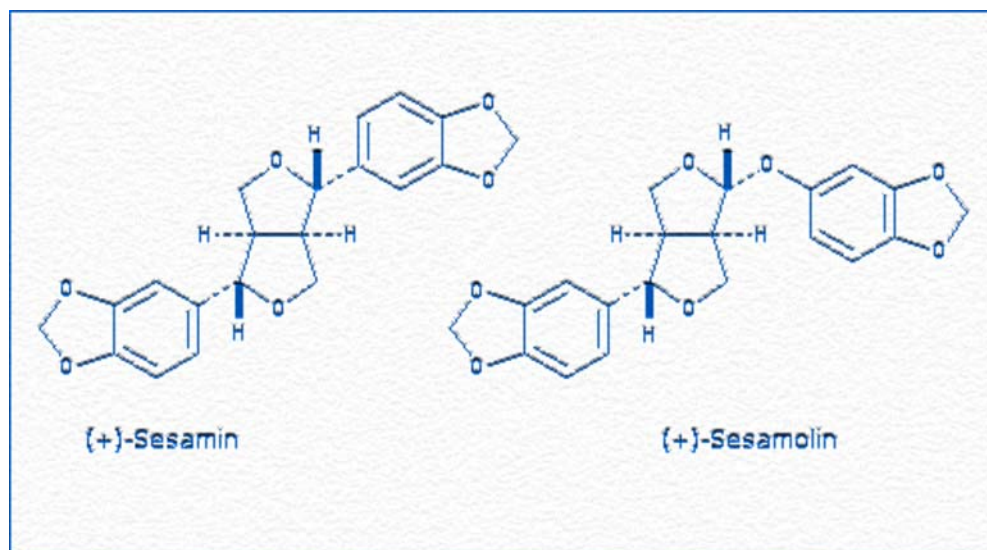
The art and science of
amateur experimentalism

Sesamin

detritus - 6-5-2008 at 16:13

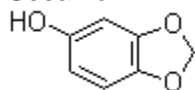
When raw sesame seed oil is washed with acetone plus water (US2467904) the potent antioxidants sesamin and sesamol can be extracted without damage to the remainder of the oil.

I know how much people love antioxidants, so I decided to post interesting structure here.



Sesamol can be hydrolyzed to sesamol in aqueous alkali, as a side note.

Sesamol:



organometallic - 8-5-2008 at 08:58

Ok so sesamol has a pretty interesting shape.. to me anyway. I want to know, would it be possible to replace the phenol OH group with a methyl group, possibly with 1-iodomethane? If so, that would produce 3,4(methylenedioxy)toluene, which I bet could be oxidised similarly to methyl benzene to produce piperonal... the hunt for vanilla flavourings has taken an interesting turn..

Anyone care to lend insight? 😊

methoxy

Tsjerk - 8-5-2008 at 09:19

If you would react sesamol with iodomethane you would get the methoxy, not the methyl. You would have to react the sesamol with HI to change the hydroxy for a iodine, and react that with something to get to the methyl.

organometallic - 8-5-2008 at 10:12

"If you would react sesamol with iodomethane you would get the methoxy, not the methyl. You would have to react the sesamol with HI to change the hydroxy for a iodine, and react that with something to get to the methyl."

Can anyone confirm that this would work? Also, anyone have any idea what "something" would react with 3,4(methylenedioxy)iodobenzene to produce 3,4(methylenedioxy)toluene?

This seems fairly promising..

12AX7 - 8-5-2008 at 10:54

Sounds like a classic Grignard.

[Edited on 5-8-2008 by 12AX7]

organometallic - 8-5-2008 at 11:13

Haha! Shit, i'm blind. Thanks.

Klute - 8-5-2008 at 11:17

HI reduction would cleave the methylenedioxy- long before iodinating the cycle... Tosylation and subsequent reduction of the tosylate (LAH, NaBH₄, [NaBH₃CN](#), H₂/Pd/C, etc would give 3,4-methylenedioxybenzene.

The NaBH₃CN procedure is for alkyl tosylate. I'm not sure if it can be applied to aryl tosylates, you would need to check that..

[Edited on 8-5-2008 by Klute]

Bolt - 8-5-2008 at 12:52

I thought that it is nearly impossible to remove a hydroxyl group from a benzene ring. I know that you can replace a halide with an -OH if there's a meta(?) deactivating group. Aryl alcohols don't react the same way aliphatic alcohols do...

stoichiometric_steve - 8-5-2008 at 14:03

Quote:

Originally posted by Klute Tosylation and subsequent reduction of the tosylate (LAH, NaBH₄, H₂/Pd/C, etc would give 3,4-methylenedioxybenzene.

and then you could just buy catechol and methylenate that. avoids extracting huge amounts of sesame oil... 😊

Klute - 8-5-2008 at 22:42

Totally agreed! But who want's piperonal in the first place 😊 And as Bolt mentionned, this could not work on phenols, I have found no direct examples (but didn't search much), so it's just a suposition..

Now what could be done is ortho-formylation of sesamol, followed by methylation of the phenol. The benzaldehyde would be a precursor to [MMDA-2](#) without the need of a Vilsmeier... The Mg/(HCHO)_n formylation should yield the right isomer. This could be higher yielding than the original procedure.

not_important - 9-5-2008 at 05:33

If you look at sesamin and pay attention to those benzylic and tertiary hydrogens, you might come up with a method to selectively attack those to give handles that end up letting you cleave the side chain and get (two) ArCHO or ArCO₂H.

But at 5 to 10 parts per thousand, you'll need a lot of sesame oil, and a bunch of messy extraction work.

LSD25 - 12-5-2008 at 02:07

Here is something interesting you can do with it if you can find it, but...

<http://jchemed.chem.wisc.edu/Journal/Issues/2006/FebACS/ACSSub/V83N...>

Now what would you describe that reaction as? It ain't a Claisen rearrangement, because it doesn't use an ether, it is not a Fries rearrangement because it doesn't use the carboxylic acid, rather it uses the dimethylbutenal, which attaches itself ortho to the phenol, doesn't bother the MD, and looks like it might be of some use (I like the way they describe the entire thing in such detail - even I couldn't fuck it up - bet I could).

Oh yeah, Klute, is this what you were thinking of?

Attachment: [PdC.DEA.Hydrodeoxygenation.phenols.pdf](#) (818kB)

This file has been downloaded 133 times

Saerynide - 12-5-2008 at 12:17

Quote:

Originally posted by not_important

But at 5 to 10 parts per thousand, you'll need a lot of sesame oil, and a bunch of messy extraction work.

You can buy Sesamin supplements I think 😊
