Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-690-RC5, 2019 © Author(s) 2019. This work is distributed under the Creative Commons Attribution 4.0 License.



Interactive comment on "Technical Note: Preparation and purification of atmospherically relevant α -hydroxynitrate esters of monoterpenes" by Elena Ali McKnight et al.

Anonymous Referee #5

Received and published: 9 September 2019

The paper by McKnight et al. presents successful synthetic routes to the preparation of the hydroxy nitrates that are produced in nature by the atmospheric oxidation of monoterpenes. In recent years it has been shown that formation of these organic nitrates are an important sink for NOx in the atmosphere, as well as an important mechanism for the production of atmospheric aerosol. Such aerosol results from an interaction between anthropogenic NOx, and biogenic monoterpenes. Thus, interestingly, control of NOx emissions (from combustion) can influence the role of production of atmospheric aerosol from biogenic emissions. There is thus considerable interest in these compounds, and their atmospheric chemistry, and, e.g. the ability to study their hydrolysis rates. However, the atmospheric chemistry community has not had much

C1

success in making these compounds, and that is a major stumbling block to progress. Here is a paper that connects the organic synthesis community to the atmospheric chemistry community in a useful way, and the atmospheric chemistry community increasingly needs this connection, in more general terms. This paper is technically important, and will stimulate a great deal of badly needed research, likely to start with atmospheric chemists at Reed. So, this paper should be published, and I think can be done with only editorial changes. That said, the authors need to be aware that the audience here is indeed atmospheric chemists, who are not versed in the editorial jargon of synthetic organic chemists. So, the paper could be made more readable and useful if the authors shed the notion that they are writing to organic chemists. They are, at best, writing to organic chemists existing with the labs of atmospheric chemistry professors.

Comments and suggested changes are listed below, in the order they arose in the manuscript.

- 1. The last sentence of the Introduction is unclear -30-40% of MT emissions are at night, or the nitrate radical consumes 30-40% of the emitted MTs at night? Please note that the OH radical oxidation pathway is still an important source of MT-nitrates, e.g. as discussed in Pratt et al., 2012.
- 2. Line 21, page 2 is there a better reference for this quite general organic chemistry laboratory hazard?
- 3. The Ma et al. paper should not be cited. If you go to the ACP web site, it says "This paper has been retracted."
- 4. Page 3, line 17 what is CPBA? (Good example of my comment above; most organic chemists will know that it doesn't stand for Certified Professional Behavioral Analyst).
- 5. Page 3, line 27 should the reference be Crocker and Grayson, 1969? And on Page

- 4, line 8.
- 6. Page 5, line 8 should be Steiner et al., 2002. And line 16.
- 7. Page 7, at 2.3.1 title, refer the Table 1 for structures. The reader needs to see the structures. Line 2 do you mean the trans-3-carene epoxide? Also on line 10, the epoxide?
- 8. Page 8, line 4, those percentages are the yields? Please try to avoid organic synthetic chemists shorthand. Also line 13. For structures 16 and 17, line 22, are there yields?
- 9. Page 8, line 24, what is "the title compound"? Also page 9, lines 4, 17, and 23. There is sloppy shorthand on this page, e.g. line 13 "the following". What following?
- 10. Line 11 you mean the a-pinene oxide? Line 17 by "title compound" you mean the aldehyde? Similarly, I find line 23 confusing. You synthesized the alcohol?
- 11. Page 10, lines 13 and 14 "The title compound", when the title compound is "Nitrate ester 23" does not make for great/easy reading. Perhaps it would be helpful that in each case, the structure should be shown next to the name, as a graphic? That would really make the paper more readable.
- 12. Page 14, line 8 provide a reference for the fast hydrolysis rates.
- 13. Page 19, line 6, re decomposition of ester 14 does this depend on water content in the solvent? Do you know what the decomposition products are? The corresponding diol?
- 14. Page 19, line 9 the "the" methods, but "successful methods".
- 15. Line 17 insert "for" after "important".

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-690, 2019.