

**Organic Synthesis in the Study of Volatile Terpenes in the
Atmosphere**

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ARTICLE

Organic Synthesis in the Study of Terpene-derived Oxidation Products in the Atmosphere

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Volatile biogenic terpenes involved in the formation of secondary organic aerosol (SOA) particles participate in rich atmospheric chemistry that impacts numerous aspects of the earth's complex climate system. Despite the importance of these species, understanding their fate in the atmosphere and determining their atmospherically-relevant properties has been limited by the availability of authentic standards and probe molecules. Advances in synthetic organic chemistry directly aimed at answering these questions has, however, led to exciting discoveries at the interface of chemistry and atmospheric science. Herein we provide a review of the current state of the literature regarding the synthesis of commercially unavailable authentic standards used to analyze the composition, properties, and mechanisms of SOA particles in the atmosphere.

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1. Introduction

Atmospheric fine particulate matter (PM_{2.5}) has been shown to scatter and/or absorb radiation, influence cloud formation and climate processes,¹⁻⁴ as well as have detrimental effects on human health.⁵⁻⁷ Organic species constitute the majority of PM_{2.5} in both pristine and urban environments.^{2, 8} Secondary organic aerosol (SOA) particles (SOA), in particular, make up a larger fraction of atmospheric organic aerosol than primary organic aerosol (POA) particles and are formed as a result of the chemical transformation of volatile organic compounds (VOCs) via atmospheric oxidation. Reactions of both biogenic and anthropogenic VOCs with atmospheric oxidants generate compounds of lower volatility, and often higher O:C ratios, which can then partition into the condensed aerosol phase, continue to react heterogeneously on existing particles, or nucleate to form new particles.⁹⁻¹⁴

Although great progress has been made toward identifying key molecular precursors that form biogenic and anthropogenic SOA, the current level of mechanistic understanding regarding the formation of SOA particles remains low. These gaps in our knowledge of the chemistry of SOA particles have resulted in difficulties in the prediction of SOA particle effects on the climate system by atmospheric chemistry and transport models,^{9, 15-17} and have thus contributed greatly to the large uncertainties in the effects of aerosols on radiative forcing and global warming.¹⁸ Furthermore, the large number as well as variability of chemical constituents, sources and chemical reactions creates numerous challenges in determining the chemistry, composition, and properties of SOA particles. For instance, it has been estimated from mass spectrometric studies that 10,000–100,000 different organic compounds have been detected in the atmosphere.^{19, 20}

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oxidation mechanisms in the atmosphere.



Ariana Gray Bé was born in Cleveland, Ohio. She received her B.S. in Chemistry from Denison University in 2015, where she worked under the direction of Prof. Joseph Reczek. She received her Ph.D. in 2020 from Northwestern University and was the recipient of an NSF Graduate Research Fellowship from 2006 to 2009. Jointly advised by Prof. Regan Thomson and Prof. Franz Geiger, her

doctoral studies focused on the synthesis and surface chemical analysis of terpene-derived oxidation products in biogenic secondary organic aerosol particles. She then spent two years in the Innovation Department at Beyond Meat, and in 2022 she joined the Research and Development team at Ambercycle, a materials company working to create an infinite textile ecosystem to eliminate waste in fashion.



Franz Geiger is currently the Charles E. and Emma H. Morrison Professor of Chemistry at Northwestern University, where he leads research projects that involve experiments and computations to study the special role that surfaces and interfaces play in the world. He is a native of Berlin, Germany, where he received his Vordiplom in chemistry at the Technische Universität in 1993.

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Jonathan Varelas was born in Madison, CT. He completed his BS in chemistry from Providence College in 2015 under the supervision of Prof. Seann Mulcahy. He then received his doctorate in chemistry from Northwestern University in 2021 as a joint student in the laboratories of Prof. Regan Thomson and Prof. Franz Geiger, where he synthesized and studied

isoprene-derived organosulfates. After completing his doctorate, Jonathan moved into the realm of science communications, operating as a freelance consultant and multimedia producer for various pharmaceutical companies. He now serves as the director of



Regan J. Thomson was born in New Zealand in 1976 and received his Ph.D. in 2003 at The Australian National University working with Prof. Lewis N. Mander. Following postdoctoral studies with Prof. David A. Evans at Harvard University, he joined the faculty at Northwestern University in 2006 where he is currently a Professor of Chemistry. Regan's research interests include reaction

development, total synthesis, natural product discovery and biosynthesis, and atmospheric chemistry. He is the recipient of an NSF CAREER Award (2009), an Amgen Young Investigator Award (2010), an Illinois Division American Cancer Society Research Scholar Award (2012), and a Novartis Chemistry Lectureship (2015–2016).

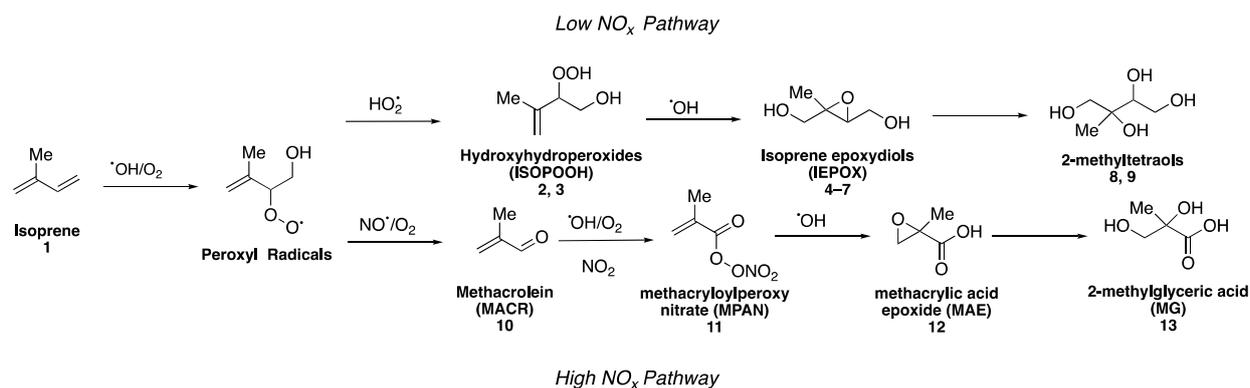


Figure 1. Atmospheric oxidation pathways for isoprene.

Over the past decade, organic synthesis has begun to emerge in the field of atmospheric chemistry as a powerful tool in the study of SOA material. While several SOA precursors and surrogate compounds, along with select oxidation products, are available from commercial sources, the majority of SOA constituents are not. Synthetic organic chemistry addresses this challenge by enabling access to authentic standards, which, when combined with physical measurements, laboratory chamber studies, and field studies, can be used to provide a molecular characterization of SOA particles.¹⁹ Indeed, pure and homogenous synthetic reference standards of compounds that are not available from commercial sources have not only proven critical for benchmarking and chemical identification in mass spectrometric studies of SOA particles, but have also provided insight into important physical properties of aerosol particles. This manuscript seeks to provide a comprehensive review of the current state of the literature regarding the synthesis of commercially unavailable authentic standards used to analyze the composition, properties, and mechanisms of SOA particles in the atmosphere. We discuss studies reporting the synthesis of molecular standards derived from biogenic SOA precursors, namely isoprene (Section 2), monoterpenes (Section 3), and sesquiterpenes (Section 4). We also discuss the synthesis of standards relevant to SOA material influenced by anthropogenic pollutants, namely organosulfates and organonitrates (Section 5), and probe compounds (Section 6) to help facilitate mechanistic investigations. Where possible, and to the best of our ability, yields are provided and structures are depicted showing relative or absolute stereochemical relationships if reported in the cited work. If the original work did not provide yields or indicate stereochemistry, none are shown.

2. Isoprene-Derived Species

Isoprene (2-methyl-1,3-butadiene, C₅H₈, **1**) is the most abundant non-methane hydrocarbon emitted into the Earth's atmosphere with emissions estimated to exceed 500 Tg yr⁻¹.²¹⁻²³ Isoprene dominates emissions from many tropical forest ecosystems as well as deciduous plants. It was originally proposed that atmospheric oxidation of isoprene yielded only highly volatile gaseous products that did not contribute to SOA

formation.^{24, 25} In 2004, however, Claeys and coworkers reported the synthesis of a mixture of the two diastereomeric compounds, 2-methylthreitol (**8**) and 2-methylerythritol (**9**), which were then used in combination with mass spectrometric studies to identify both compounds in field aerosol samples collected in a pristine environment in the Amazon rainforest (Figure 1).²⁶ While detailed synthesis procedures were not provided, this groundbreaking work tied the formation of low volatility oxidation products formed in the aerosol phase under low nitrogen oxide (NO_x = NO + NO₂) concentrations (generally considered to be pristine conditions) to the photooxidation of isoprene, resulting in a rapid growth of studies aimed at understanding the role of isoprene-derived aerosol particles in the climate system.

Isoprene (**1**) predominantly reacts with hydroxyl (OH) radicals in the atmosphere, which, along with slower oxidation by nitrate (NO₃) radicals and ozone (O₃), accounts for up to 50% of the global SOA budget.²⁷⁻³⁰ Oxidation of isoprene by OH radicals results in the formation of peroxy radicals (RO₂), which can react with other atmospheric oxidants to form organic compounds that contribute to SOA formation (Figure 1). In the presence of higher concentrations of NO_x (a marker for anthropogenic pollution due to combustion processes), these radicals can decompose to form smaller volatile products, such as formaldehyde and methyl vinyl ketone, which results in minimal amounts of SOA particles.^{10, 30-32} Other studies using high NO_x conditions have demonstrated that isoprene SOA particles can also form from the oxidation of a variety of isoprene-derived intermediates, including methacrolein (MACR, **10**) and methacryloylperoxynitrate (MPAN, **11**).^{31, 33-36} In the absence of NO_x, these radicals can react with hydroperoxy radicals (HO₂) to form various isomers of isoprene hydroxyhydroperoxides (ISOPOOH, **2** and **3**),³⁷ which then go on to form isomeric isoprene epoxydiols (IEPOX) compounds (**4-7**). These epoxides have been proposed as key intermediates in the formation of biogenic SOA particles.^{33, 38-41} Acid-catalyzed uptake and multiphase chemical reactions of epoxide compounds as well as aqueous reactions of MACR (**10**) and methyl vinyl ketone with sulfate radical anions have been shown to enhance isoprene-derived SOA formation.^{33, 35, 42-44} Recent studies have led to the development of a variety of syntheses of authentic standards of intermediates in the atmospheric isoprene oxidation pathway. These standards have

been essential in the characterization of isoprene-derived SOA particles and have yielded valuable insight into SOA formation and growth, as outlined in the sections below.

2.1 Isoprene Hydroxyhydroperoxides (ISOPOOH)

As previously mentioned, ISOPOOH isomers (**2**, **3**) are considered to be some of the first pristine reaction products formed from the reaction of isoprene with HO₂. These hydroperoxides have very different properties compared to their urban counterparts formed under high concentrations of NO_x.^{45, 46} Atmospheric models estimate that only 30% of global emissions of isoprene react with NO_x, emphasizing the abundance of ISOPOOH and other intermediates formed under low NO_x conditions.^{38, 45, 47} The use of synthetic ISOPOOH has only appeared in the literature in the past few years, with the first report in 2014, although this report and others do not include specific synthesis details.⁴⁸ Various organic synthetic studies have, however, used photooxygenation (*via* an ene reaction), as well as more recent synthetic methodology involving oxidation by H₂O₂ catalyzed by phosphomolybdic acid (PMA)^{49, 50} to access similar peroxides.^{51, 52} Chamber experiments involving ISOPOOH isomers, 2-hydroperoxy-3-methyl-but-3-en-1-ol (4,3-ISOPOOH, **2**) and 2-hydroperoxy-2-methylbut-3-en-1-ol (1,2-ISOPOOH, **3**),^{38, 53, 54} revealed that reactions with OH radicals can lead to the production of IEPOX at yields greater than 75%.⁵³ ISOPOOH standards were also used to demonstrate that products directly derived from ISOPOOH have the potential to form SOA compared to highly oxidized compounds detected in monoterpene oxidation.⁵⁴ Access to a synthetic standard also allowed for direct studies of its uptake under atmospheric conditions, which revealed that uptake is slow and reduced by the presence of surface-active organic species on the surfaces of aerosols.^{41, 55, 56} Chamber experiments using authentic ISOPOOH standards (**2**, **3**) also revealed an additional route to SOA formation that does not proceed through the formation of the IEPOX intermediate.^{56, 57} These standards continue to be used in both field and chamber studies to better quantify ISOPOOH in the atmosphere and characterize SOA formation pathways from isoprene.^{48, 58-62}

2.2 Isoprene-Derived Epoxy Diols (IEPOX)

Gas-phase IEPOX isomers (**4**–**7**) form from the oxidation of ISOPOOH in the atmosphere and laboratory studies indicate that these compounds are likely key intermediates in the production of low volatility products in SOA material derived from isoprene under low NO_x conditions.^{33, 38, 39, 63, 64} IEPOX was first detected in 2009 through the synthesis of a surrogate standard (2,3-epoxy-1,4-butanediol, BEPOX) lacking the methyl group present in IEPOX, since authentic standards of IEPOX had not yet been accessed. By quantifying IEPOX using the synthetic BEPOX standard, this important study established that OH-initiated oxidation of isoprene gave high yields (~50%) of IEPOX and suggested that IEPOX may serve as a precursor to the formation of 2-methyltetraols, C₅-alkene triols, dimers, and organosulfates.³⁸

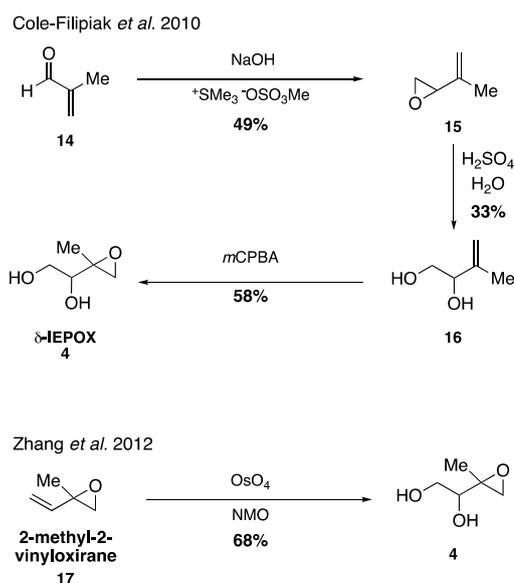


Figure 2. Synthesis of δ -IEPOX (**4**).

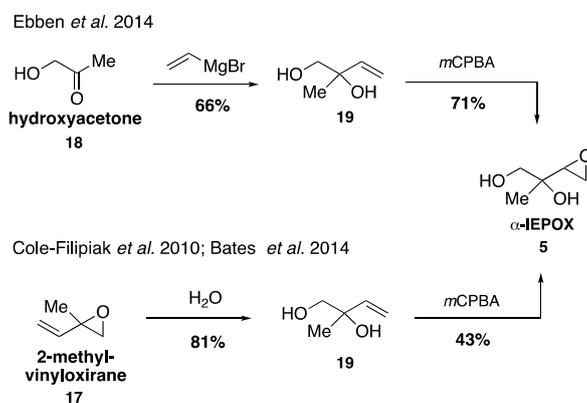


Figure 3. Synthesis of α -IEPOX (**5**).

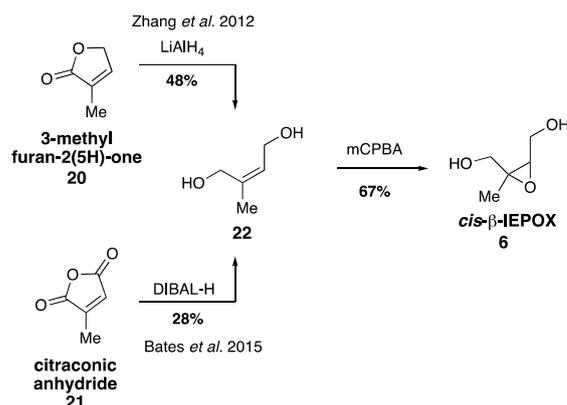


Figure 4. Synthesis of *cis*- β -IEPOX (**6**).

While syntheses of two isomers of IEPOX were previously reported in synthetic organic literature,⁶⁵⁻⁶⁷ the first authentic isomers of IEPOX were synthesized and used in atmospheric studies in 2010 (Figure 2).⁶⁷

Synthesis of three different isomers of IEPOX confirmed that hydrolysis lifetimes of epoxides in the atmosphere are on the order of SOA lifetimes at atmospherically relevant pH values,⁶⁷

improving upon similar studies using surrogate compounds.⁶³ While the first syntheses resulted in a mixture of IEPOX isomers, optimization of synthetic routes towards the various isomers of IEPOX in recent years has resulted in a rapid growth of studies using synthetic standards of IEPOX in order to quantify its abundance in the environment as well as analyze effects of atmospheric conditions on its role in SOA formation through both chamber and field studies.^{32, 39-41, 68-73} Of the four isomers, δ -IEPOX (**4**) is the most easily accessed (**Figure 2**).

While it was originally synthesized in three separate steps from methacrolein (**14**) in 2010,⁶⁷ subsequent syntheses accessed δ -IEPOX (**4**) in one step through the dihydroxylation of commercially available 2-methyl-2-vinylloxirane (**17**).⁷⁴ α -IEPOX (**5**) can be accessed in two steps either from 2-methyl-2-vinylloxirane (**17**) via epoxide opening under aqueous conditions followed by epoxidation, or from hydroxyacetone (**18**) via a vinyl Grignard reaction followed by epoxidation (**Figure 3**).⁷⁴⁻⁷⁶ *cis*- β -IEPOX (**6**) can also be accessed in two steps through the reduction of 3-methyl furan-2(5H)-one (**20**) or citraconic anhydride (**21**), followed by epoxidation (**Figure 4**).^{74, 75, 77} Synthetic routes were also established to access isomeric tetrahydrofurans (**Figure 5, 23 and 24**), which were detected as rearrangement products of IEPOX isomers in acidic aerosols during chamber experiments.^{39, 74, 78} A mixture of *cis*- and *trans*-methyltetrahydrofurans (**22, 23**) can also be accessed in four steps from dihydroxytetrahydrofuran (**25**) and then separated to access the pure isomers by column chromatography.⁷⁴

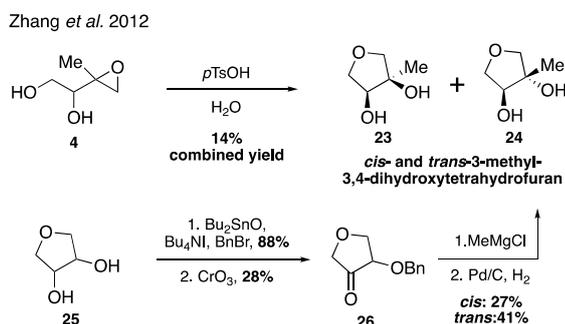


Figure 5. Synthesis of tetrahydrofurans **23** and **24**.

Trans- β -IEPOX (**7**) requires the greatest number of synthetic steps out of all the epoxides, but access to standards of all four isomers has determined that it is the longest-lived and most abundant isomer in the atmosphere (**Figure 6**).^{76, 79} *Trans*- β -

IEPOX (**7**) can be accessed in four steps from isoprene (**1**) by a procedure involving initial bromination, hydrolysis and epoxidation,⁶⁷ or in five steps from 3-methyl-2-buten-1-ol (prenol, **30**)^{74, 75} by a route involving allylic oxidation followed by epoxidation. Synthetic *trans*- β -IEPOX (**7**) was observed to have enhanced surface activity and was tentatively identified on the surfaces of isoprene-derived laboratory aerosols using a surface-specific vibrational spectroscopy technique, sum frequency generation (SFG) spectroscopy.^{75, 80} These results indicate that higher concentrations of *trans*- β -IEPOX at the surfaces of aerosols may significantly decrease supersaturation ratios and increase the propensity of SOA to form cloud condensation nuclei (CCN). Additional studies have shown that uptake of *trans*- β -IEPOX (**7**) at the surface of aerosols accounts for half of the particle-phase material produced from isoprene photooxidation in chamber studies.⁷⁹ Access to greater quantities of each of the IEPOX isomers has led to a more detailed understanding of their physical properties, their rates of chemical reactions with other atmospheric constituents, and has also allowed for further identification of higher order oxidation products in the atmosphere.^{55, 60, 67, 68, 75, 76, 79-82}

2.3 2-Methyltetraol Diastereomers

Since their first synthesis in the atmospheric community in 2004, 2-methyltetraol standards have been used ubiquitously in atmospheric studies and have been recognized as definitive markers of aerosols derived from isoprene detected in a variety of regions.^{26, 31, 64, 83-89} While the first synthetic route towards these standards yielded a mixture of the two diastereomers 2-methylthreitol (**8**) and 2-methylerythritol (**9**), additional routes have since been developed to access pure standards of each possible stereoisomer.

Prior to studies involving the atmospheric chemistry of 2-methyltetraols, an enantioselective synthesis of 2-methylthreitol (**8**) and 2-methylerythritol (**9**) was published in 2000 in order to investigate their biosynthesis in plant terpenoids (**Figure 7**).⁹⁰ 2-Methylthreitol (**8**) and 2-methylerythritol (**9**) were synthesized in six and seven steps, respectively, from dimethylfumarate (**33**).⁹⁰ For the case of compound **8**, control of absolute stereochemistry was achieved using a Sharpless epoxidation of allylic alcohol **34** to deliver epoxide **35** with high enantioselectivity (93:7 er). Epoxide

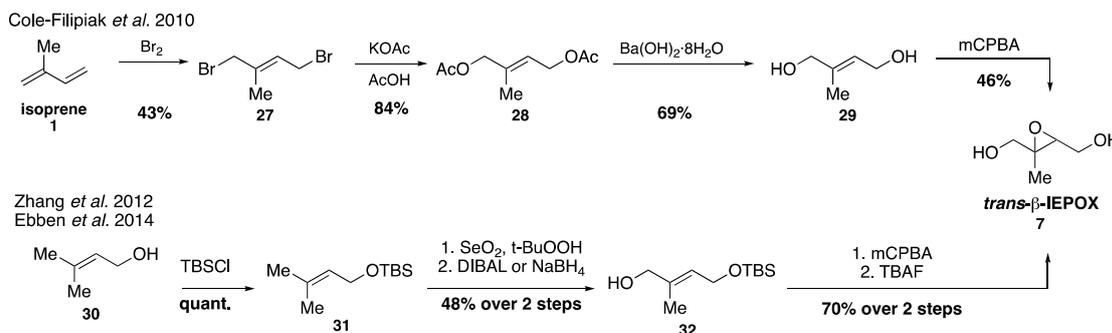


Figure 6. Syntheses of *trans*- β -IEPOX (**7**) from either isoprene (**1**) or prenol (**30**).

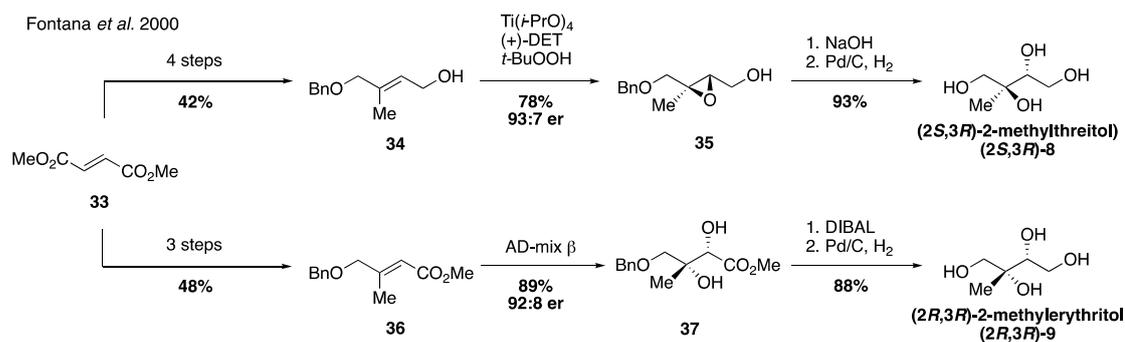


Figure 7. Enantioselective synthesis of the diastereomeric 2-methyltetraols.

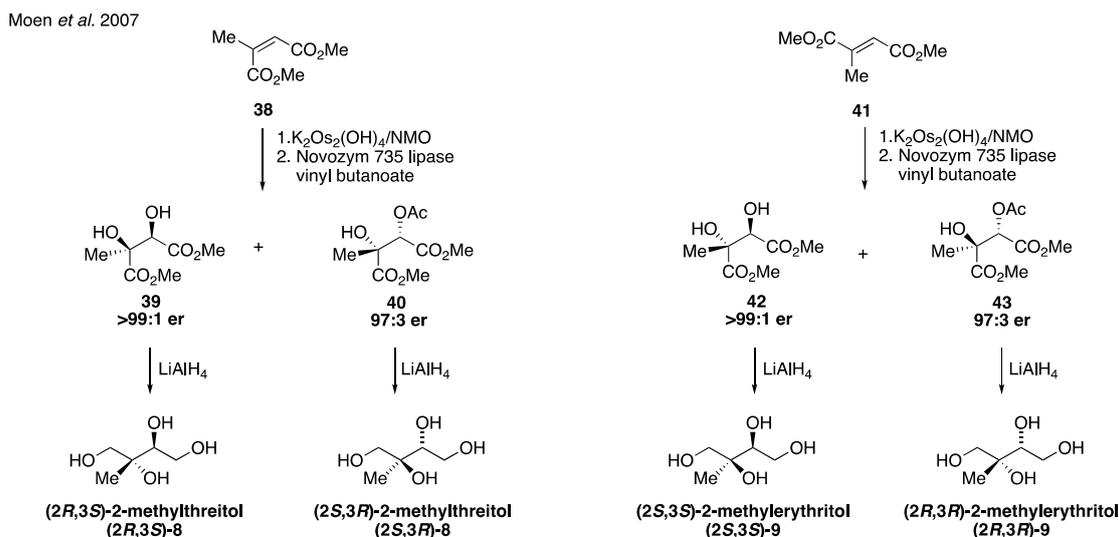


Figure 8. A chemoenzymatic approach to accessing all stereoisomers of the 2-methyltetraols.

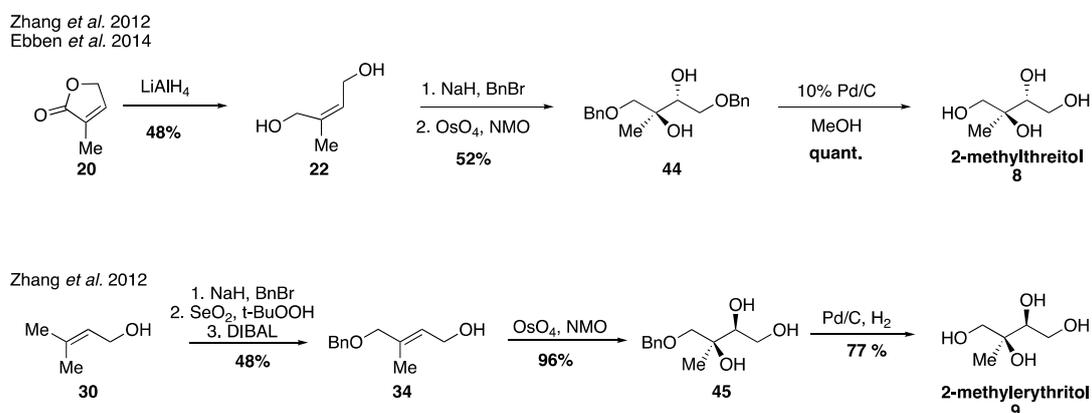


Figure 9. Efficient access to racemic 2-methyltetraols that fueled atmospheric chemistry studies.

opening and debenzoylation delivered the optically enriched tetraol (2*S*,3*R*)-2-methylthreitol (**8**). Enantioselective access to the diastereomeric tetraol **9** was accomplished through a Sharpless dihydroxylation of enoate **36**, which produced diol **37** in a 92:8 ratio of enantiomers. Reduction of the ester and cleavage of the benzyl ether yielded optically enriched (2*S*,3*R*)-2-methylerythritol (**9**). Several years later, in 2007, Moen and coworkers established a chemoenzymatic route that provided

access to all four stereoisomers of the methyltetraol compounds through an enantioselective resolution (**Figure 8**).⁹¹ Access to all four of these isomers was highly valuable and enabled subsequent studies determining enantiomeric compositions in atmospheric aerosols.^{92, 93} Additional synthetic work fueling further atmospherically-relevant research focused on efficient routes to racemic material (**Figure 9**), generating 2-methylthreitol (**8**) in four steps from 3-methyl furan-2(5H)-one (**20**) and 2-methylerythritol (**9**)

in five steps from 3-methyl-2-buten-1-ol (**30**).⁷⁵ Access to these standards continues to aid in the study of isoprene oxidation products formed under low NO_x conditions and their quantification in field and chamber studies.^{33, 36, 39, 63, 67}

2.4 Isoprene-derived C₅H₁₀O₃ Products

Reactive uptake products possessing the molecular formula C₅H₁₀O₃ have served as tracers for the study of isoprene-derived SOA, but the structural identity of these species has remained elusive until recently. In order to provide authentic standards of two possible C₅H₁₀O₃ candidates the Gold lab established synthetic routes to access unsaturated triol **46** and hemiacetal **51** (Figure 10).

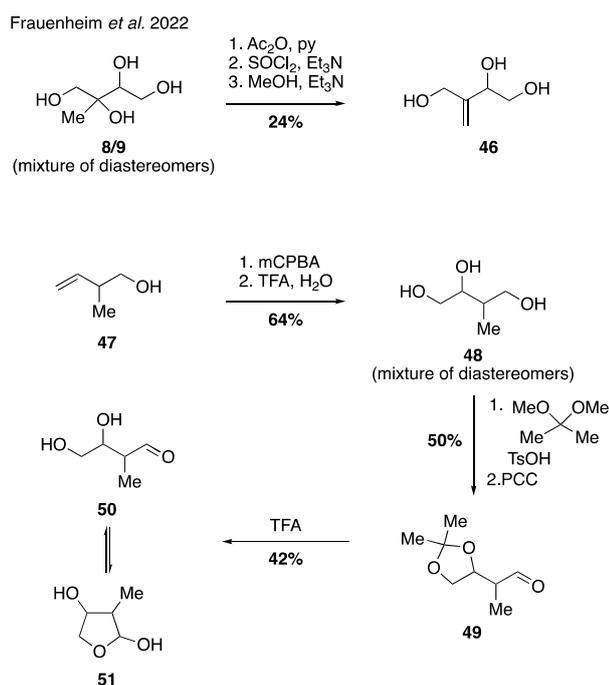


Figure 10. Synthesis of “C₅H₁₀O₃” products.

The synthesis of triol **46** was conducted using a mixture of 2-methyltetraol diastereomers (i.e., **8/9**) as the starting material, which was first treated with acetic anhydride to protect the less hindered primary and secondary alcohols. Dehydration of the free tertiary alcohol using thionyl chloride followed by removal of the acetate protecting groups produced the desired triol **46** in good overall yield, albeit as a mixture of diastereomers. The synthesis of hemiacetal **51** commenced from alkene **47**, which underwent epoxidation and hydrolysis to yield triol **48**. Preferential formation of the 5-membered cyclic acetonide followed by oxidation using PCC delivered aldehyde **49**, which was treated with trifluoroacetic acid to cleave the protecting group. Analysis of the NMR spectral data of the product showed no diagnostic aldehyde resonances associated with the open-tautomer **50**, indicating an equilibrium strongly favoring the cyclic hemiacetal **51**. Access to these two authentic standards allowed confirmation of their presence in laboratory-generated IEPOX SOA and in atmospheric SOA samples. Quantitation of chamber-derived yields led the authors to tentatively estimate

that these C₅H₁₀O₃ isomers could contribute 8.7 Tg C yr⁻¹ to the atmosphere.

2.5 Methacrolein-Derived Oxidation Products

Emission of NO_x from anthropogenic sources can alter the oxidation pathways of biogenic VOCs in the atmosphere. Laboratory experiments have confirmed that under high NO_x conditions, essentially all SOA material derived from isoprene originates from photochemistry of its first generation oxidation product, methacrolein (MACR, **10**).^{33, 39, 94-96} Oxidation of MACR (**10**) forms methylglyceric acid (MG, **13**) and methacrylic acid (**52**), which have both been detected in both laboratory and field SOA samples.^{31, 36, 97-99} Methacrylic acid epoxide (MAE, **12**) was also identified as a precursor to the formation of MG (**13**).¹⁰⁰ Access to synthetic standards of many of these oxidation products has allowed for detailed studies on the mechanisms leading to formation of **13** as well as other dimers, oligomers, and organosulfates or nitrates that are structurally related to MG and detected in aerosol samples.^{39, 101-106}

The commercial availability of methacrylic acid (**52**) has facilitated the synthesis of higher order oxidation products derived from methacrolein (Figure 11). MG (**13**) was first prepared from methacrylic acid (**45**) using H₂O₂ and sulfuric acid,¹⁰⁷ and later using H₂O₂ and H₂WO₄.¹⁰⁸ Epoxidation of methacrylic acid (**52**) resulted in the isolation of MAE (**12**), from which MG was also accessed via acid-catalyzed hydrolysis of **12**.¹⁰⁹ MAE (**12**) has also been synthesized in two steps from benzyl methacrylate (**53**) via epoxidation followed by hydrogenation.¹⁰⁰

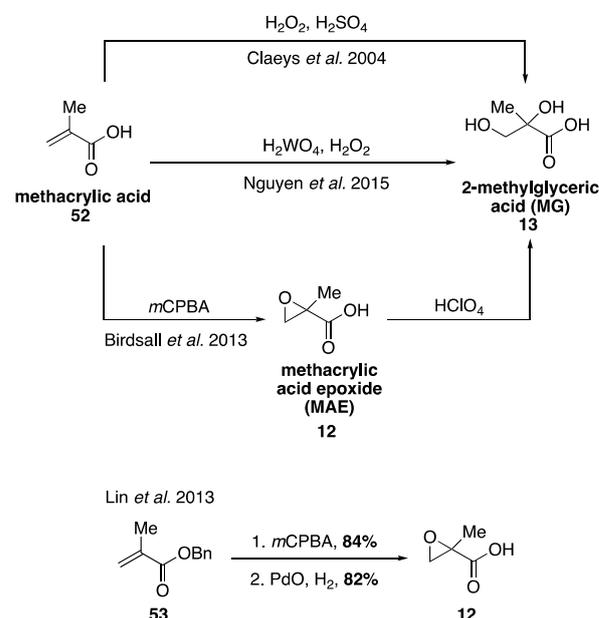


Figure 11. Synthesis of methacrolein-derived oxidation products.

2.6 2-Methyl-3-buten-2-ol (MBO)

2-Methyl-3-buten-2-ol (MBO, **54**) is a structurally similar BVOC to isoprene that is emitted by a few specific species of pine tree and has been demonstrated to contribute to photooxidation chemistry in the atmosphere.^{110, 111} Estimates of global MBO

emissions are only around 1.2–2.2 Tg yr⁻¹,^{23, 112} however MBO has been shown to affect local production of ozone and hydroxyl radicals in some forested areas.¹¹³ Major oxidation products detected in SOA constituents formed from the photooxidation of MBO (**54**) include 2-hydroxy-2-methylpropanal, glycoaldehyde, 2,3-dihydroxyisopentanol (DHIP, **56**), and MBO-derived organosulfates.^{114–117} Glycoaldehyde can undergo further oxidation to form glyoxal products, which have been shown to contribute to SOA formation.^{118–121} SOA formation from MBO photooxidation is also enhanced at higher aerosol acidities and inhibited in the presence of nitric oxide.^{39, 116, 117} Ozonolysis of MBO has been shown to form only very slight amounts of aerosols (with yields less than 1%).¹²²

MBO (**54**) is commercially available and has been used to synthesize MBO epoxide ((3,3-dimethyloxiran-2-yl)methanol, **55**) through epoxidation using *m*CPBA (**Figure 12**).¹¹⁵ Access to MBO epoxide **55** allowed for the study internal hydrogen transfer (H-shift), which may lead to the formation of epoxides.^{115, 123} Synthesis of MBO-derived epoxide **55** also enabled studies for the reactive uptake of MBO epoxide resulting in SOA formation as well as detailed studies on the formation of organosulfates and organonitrates from MBO.^{115, 124} DHIP (**56**) was also later synthesized from MBO epoxide using HClO₄.¹²⁴

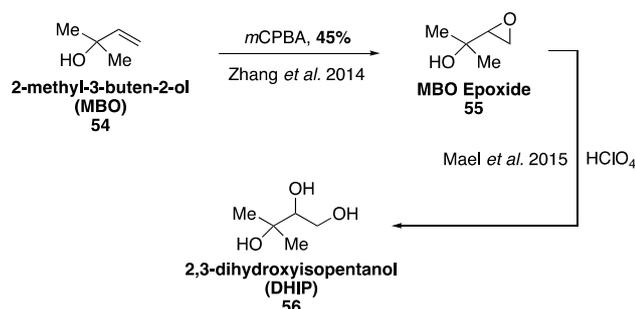


Figure 12. Synthesis of MBO-derived oxidation products.

pathways to higher order dimers and oligomers remain elusive.^{136–140} Recently, a class of extremely low-volatility VOCs (ELVOCs) was identified as an important component of aerosols derived from α -pinene ozonolysis.^{141–143} However, structural identification of ELVOCs and their formation are still uncertain and syntheses of authentic standards for these proposed products have not yet been reported.

Other abundant monoterpenes in the atmosphere whose oxidation products also contribute to SOA formation include β -pinene, limonene and 3-carene with emissions of 18.9, 11.4, and 7.1 Tg yr⁻¹, respectively.²³ A variety of authentic standards of oxidation products derived from α -pinene and β -pinene have been synthesized and aided in the identification and quantification of SOA constituents in both laboratory and field studies. While there are several studies focused on the characterization of SOA derived from limonene and 3-carene, only a few have used authentic synthetic standards to identify oxidation products.^{125, 144–150} Here we focus on the synthetic chemistry of pinene-derived oxidation products, which is much more developed.

3.1 α -Pinene- and β -Pinene-Derived Oxidation Products

Pinonaldehyde (**59**) was identified early on as a major first generation oxidation product of α -pinene ozonolysis and was first synthesized as a standard for atmospheric studies in 1997 via cleavage of commercially available pinanediol (**58**) using periodic acid (**Figure 13A**).¹⁵¹ A shorter synthetic route involves ozonolysis of α -pinene with a reductive workup.¹⁵² Pinonaldehyde (**59**) was identified as the most abundant compound in SOA particles collected over Boreal forests and has been used ubiquitously in field and chamber studies.^{153–159} Yields of pinonaldehyde (**59**) from oxidation of α -pinene (**57**) are proposed to be as high as 87%,^{160, 161} and access to

3. Monoterpene-Derived SOA Material

Monoterpenes represent an important fraction of VOCs emitted from biogenic sources in the atmosphere, with global emission rates estimated to be over 150 Tg yr⁻¹.²³ The lifetime of monoterpenes is quite short due to rapid reactions with hydroxyl radicals (OH), nitrate radicals (NO₃), and ozone (O₃), generating a complex mixture of products including carbonyls, alcohols, and carboxylic acids.^{9, 125, 126}

The most abundant monoterpene emitted in the troposphere is α -pinene (**57**, 66.1 Tg yr⁻¹), with dominant emissions from coniferous trees in Boreal forests.^{23, 127} Ozonolysis of α -pinene is an important reaction pathway,¹²⁶ with ozone accounting for approximately 40% conversion of α -pinene emitted in the atmosphere.¹²⁸ The oxidation of α -pinene by ozone has become one of the most well studied SOA systems in the atmospheric community.^{129–135} A variety of multifunctional gas phase and particle phase products have been identified, however

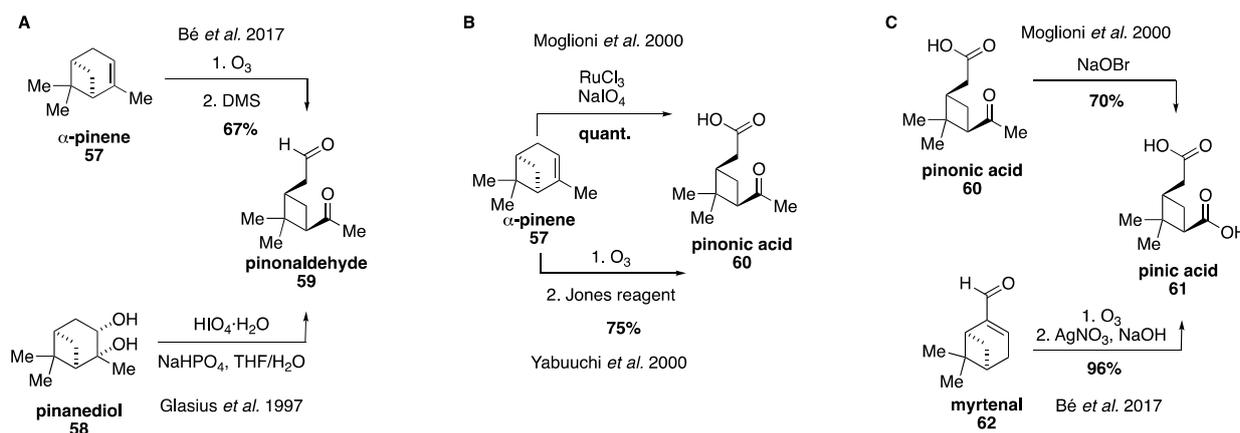


Figure 13. Synthetic access to pinonaldehyde, pinonic acid, and pinic acid.

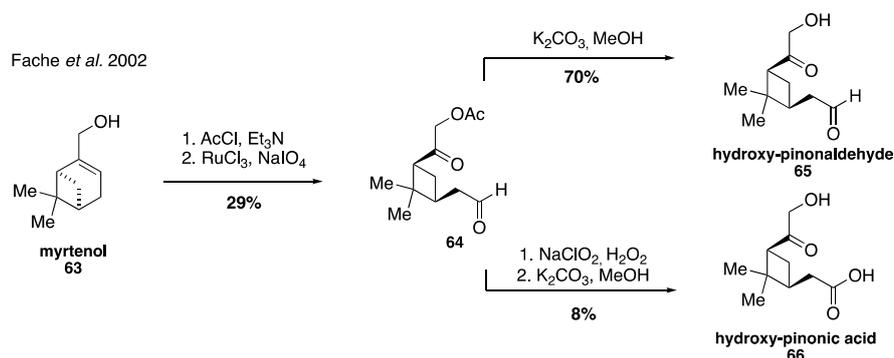


Figure 14. Synthetic access to hydroxyl-pinonaldehyde and hydroxy-pinonic acid.

pinonaldehyde (**59**) has allowed for detailed investigations of its reactivity and physical properties.¹⁶²⁻¹⁶⁶

Both pinonic acid (**60**) and pinic acid (**61**) have been identified as atmospheric tracers for α -pinene oxidation and both are commercially available.¹⁶⁷ However, synthetic routes to access each compound have also been developed, which can provide access to more pure samples (Figure 13B and 13C).^{146, 168, 169} Pinonic acid (**60**) can be accessed through ruthenium-catalyzed oxidative cleavage¹⁶⁸ or ozonolysis of α -pinene (**57**) followed by an oxidative workup.¹⁷⁰ Pinic acid (**61**) has been previously synthesized through degradation of methyl ketone **60** using aqueous sodium hypobromite,¹⁶⁸ as well as via ozonolysis of myrtenal (**62**).¹⁵² These compounds have also been used as surrogate standards to identify organic acids and dimers derived from α -pinene since authentic standards have not yet been synthesized.^{131, 171} Recent work has expanded on these efforts by focusing on the synthesis of α -pinene-derived norpinic and norpinonic acids,¹⁷² as well as peroxy-pinonic acids as proxies for highly oxygenated molecules in biogenic SOA.¹⁷³ For instance, in 2018, a mixture of dperoxy-pinonic acid and two different monoperoxy-pinonic acids was synthesized from pinic acid (**55**), however, no separation of the peroxy acids was performed, likely due to the instability of such compounds.¹⁷³ Moreover, recently, α -pinene-derived α -acyloxyalkyl hydroperoxides have been accessed via ozonolysis of α -pinene (**57**) in the presence of an excess amount of various organic acids.^{14, 174}

Hydroxy-pinonaldehyde (**65**) and hydroxy-pinonic acid (**66**) are also oxidation products that are proposed to form from more

highly substituted Criegee radicals during ozonolysis of α -pinene.¹³⁰ Both compounds have been detected in numerous field and chamber aerosol studies^{131, 175-180} and were first synthesized in 2002 from the oxidative cleavage of myrtenol (**63**), exploiting aldehyde **64** as a common intermediate (Figure 14).¹⁸¹

Lactone-containing terpenic acids derived from α -pinene and β -pinene have recently attracted a great deal of attention due to their potential relevance in dimer formation as well as other high-MW SOA products.^{131, 134, 135, 182, 183} They were first detected in 2009 through the use of authentic synthetic standards.¹²⁹ Terpenylic acid (**68**) can be prepared starting from pinonic acid (**58**) by treatment with sulfuric acid, which results in the rearrangement product, homoterpenyl methyl ketone (**67**), which can then be oxidized to form terpenylic acid (**68**) using KMnO_4 (Figure 15A).¹²⁹ Recently, an alternative procedure was reported for the direct synthesis of terpenylic acid (**68**) by oxidative cleavage of cyclopentene **69**.¹⁸⁴ Campholenic aldehyde (**71**) has been synthesized in the literature through a ZnBr_2 -catalyzed rearrangement of α -pinene oxide (**70**) in refluxing toluene (Figure 15B).^{185, 186} These synthetic standards were used to determine that terpenylic acid (**68**) forms from the reaction of atmospheric ozone with α -pinene (**57**) and campholenic aldehyde (**71**). Reaction of ozone with α -pinene (**57**) leads to the formation of α -pinene oxide (**70**), which undergoes rearrangement to generate campholenic aldehyde (**71**).¹⁸⁵ Once formed, campholenic aldehyde (**71**) can further

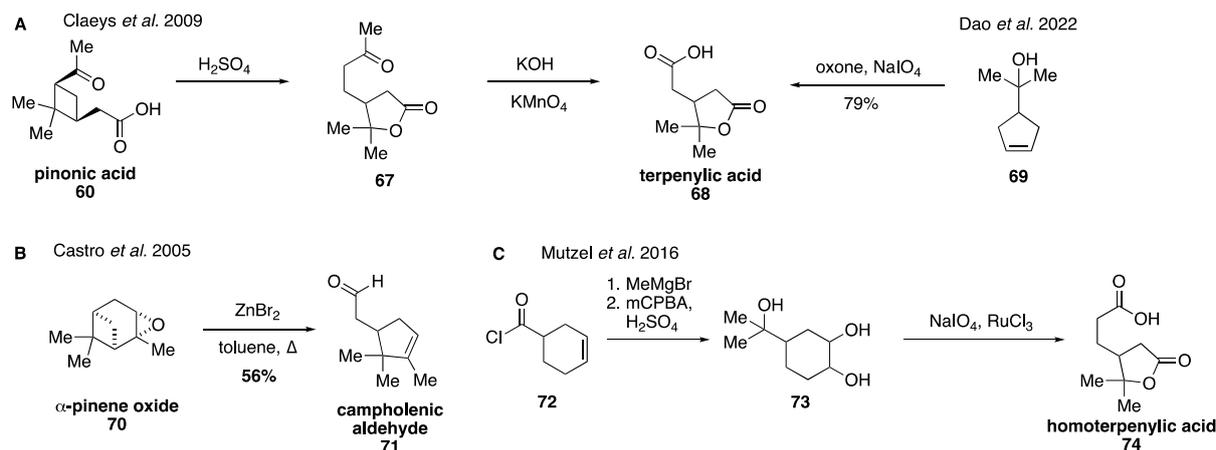


Figure 15. Synthetic access to terpenylic acid, campholenic aldehyde, and homoterpenylic acid.

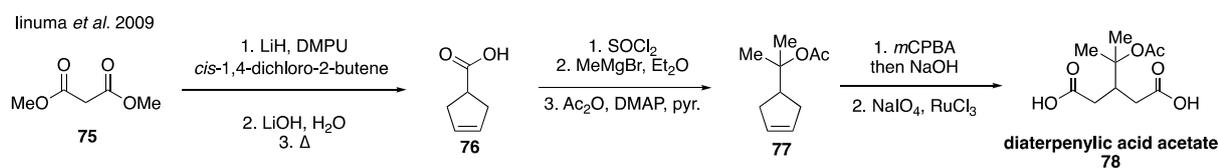


Figure 16. Synthesis of diaterpenylic acetate.

react with ozone to form terpenylic aldehyde, which forms the corresponding acid upon additional oxidation.^{187, 188}

Homoterpenylic acid (**74**) was accessed in three steps from 3-cyclohexene-1-carbonyl chloride (**72**) through a series of oxidations (Figure 15C).¹⁴⁷ In addition to these species, diaterpenylic acid acetate (**78**) was also accessed synthetically for atmospheric studies and identified as products formed from both photooxidation and ozonolysis of α -pinene.^{129, 134, 189} Diaterpenylic acid acetate (**78**) was synthesized in eight steps starting from dimethyl malonate (**75**) (Figure 16).¹⁸³ A modification on this route was reported recently, which included more detailed experimental conditions.¹⁹⁰ Access to these synthetic standards revealed that an abundant MW 358 dimer compound detected in field and chamber studies^{140, 191-194} may be a dimeric compound formed from pinic acid and terpenylic acid (or related terpenoic acids).^{129, 134}

Routes to other highly oxidized and polar species derived from pinene have also been reported (Figure 17). Hydroxycarboxylic acids have been identified as tracers for the photooxidation of α -pinene.^{84, 195, 196} 2-Hydroxy-4-isopropylhexanedioic acid was also identified in atmospheric aerosols as a higher order reaction product derived from pinic acid (**61**). Its structural elucidation was achieved through the synthesis of the ethyl diester derivative **84**, which can be formed in four steps from acid **74** (Figure 17A).¹⁹⁵ 3-MBTCA (3-methyl-1,2,3-butanetricarboxylic acid, **88**) is formed by photooxidation of *cis*-pinonic acid (**58**) and its structure was unambiguously identified through the synthesis of an authentic standard in 2007.¹⁹⁵ However, it was first detected from aerosol samples from Amazonia and Belgium in 2000 and 2002.^{197, 198} 3-MBTCA (**88**) can be generated in two synthetic steps through the nucleophilic reaction between methyl-2-bromoisobutyrate (**85**) with dimethylsuccinate (**86**) to form the trimethyl ester **87**,

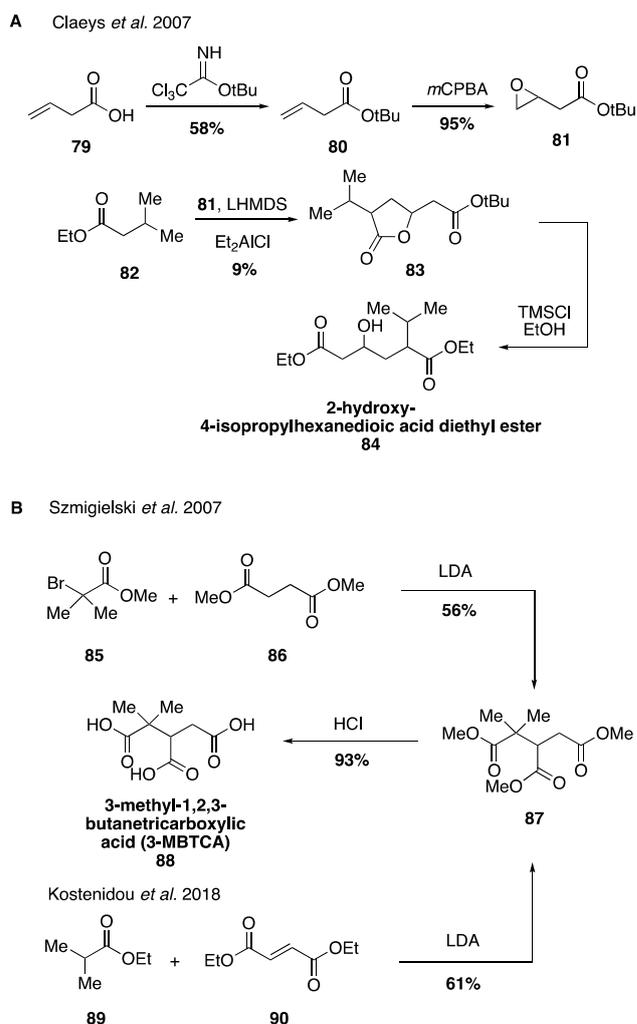


Figure 17. Synthesis of highly oxidized species.

which can undergo acid hydrolysis to yield the authentic standard of 3-MBTCA (**Figure 17B**).¹⁹⁹ Alternatively, triester **87** may be accessed by the conjugate addition of ethyl isobutyrate (**89**) to diethyl fumarate (**90**) in a more efficient manner.^{190, 200} Since its synthesis, 3-MBTCA (**88**) has been used in a variety of field and chamber studies as a tracer for the chemical aging of biogenic SOA particles by OH radicals and its formation mechanism from *cis*-pinonic acid has been studied in detail.²⁰¹⁻²⁰³

In a recent report investigating the physicochemical properties of several pinene-derived oxidation products, Szmigielski and coworkers reported a concise synthesis of terebic acid (**92**) from diethyl acetylsuccinate (**91**, **Figure 18**).¹⁹⁰ Access to this compound allowed a detailed investigation into its thermal properties, water solubility and acidity.

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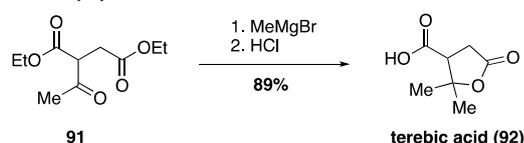


Figure 18. Synthesis of terebic acid.

3.2 α -Pinene-derived Dimers

An increasing number of field and laboratory studies have reported that α -pinene-derived dimers and higher order oxidation products formed from accretion reactions may make up a significant portion of the total organic mass present in atmospheric aerosol.^{171, 204, 205} However, the diversity of monomer precursors and the chemical transformations that couple them together presents a great challenge for structural elucidation and analysis of their relevant properties.^{194, 206-208} As such, the vast majority of dimers and oligomers derived from α -pinene, such as those proposed to form via aldol, ester, or anhydride pathways, have yet to be synthesized. Two recent studies, however, have provided initial examples of synthetic

pathways leading to pinene-derived dimers to fuel investigations in to their physical properties. The first of these reports established access to three ester dimers (i.e., **96**, **97** and **98**) using (+)-*cis*-pinonic acid (**60**) as a starting material (**Figure 19**).²⁰⁹ Diacid **93** was prepared by oxidation of the methyl ketone within **60**, while a Steglich esterification of **60** followed by reduction delivered benzyl ester **94**. Secondary alcohol **95** was accessed from **60** by reduction with sodium borohydride. Both **94** and **95** were formed as mixtures of epimeric alcohols of which the major isomer was used for subsequent reactions, but whose stereochemistry was not assigned. Benzyl ester **94** was coupled with either **93**, **60** or **95** to deliver ester dimers **96**, **97** and **98**, respectively. While these three pinene-derived esters are not thought to be naturally occurring in the atmosphere they served as useful model compounds to investigate the effect of different functional groups and molecular size on the efficiency of electrospray ionization mass spectrometry (ESI-MS) applied to monoterpene SOA material. The authors found that the ionization efficiencies of the dimer species were 19–36 times higher than *cis*-pinonic acid itself, providing evidence suggesting that the mass contribution of pinene dimers to the fraction of SOA material has been significantly overestimated in prior studies.

The second study on pinene-derived dimers targeted both aldol and ester-based dimers with the specific goal of investigating the influence that backbone stereochemistry might have on the physical properties of the compounds (**Figure 20**). Access to each of the aldol diastereomers **100** and **101** was accomplished from protected pinonaldehyde derivative **99** through the use of Paterson's procedure for stereocontrolled aldol reactions via (–)-B-chlorodiisopinocampheylborane [(–)-DIP-Cl] derived boron enolates.^{210, 211} Thus, aldol reaction of **99** with either one of the enantiomers of pinonaldehyde provided efficient access to either **100** or **101** in a stereodivergent manner (**Figure 20A**). In a similar fashion, stereodivergent synthesis of the ester-linked dimers commenced from (–)-

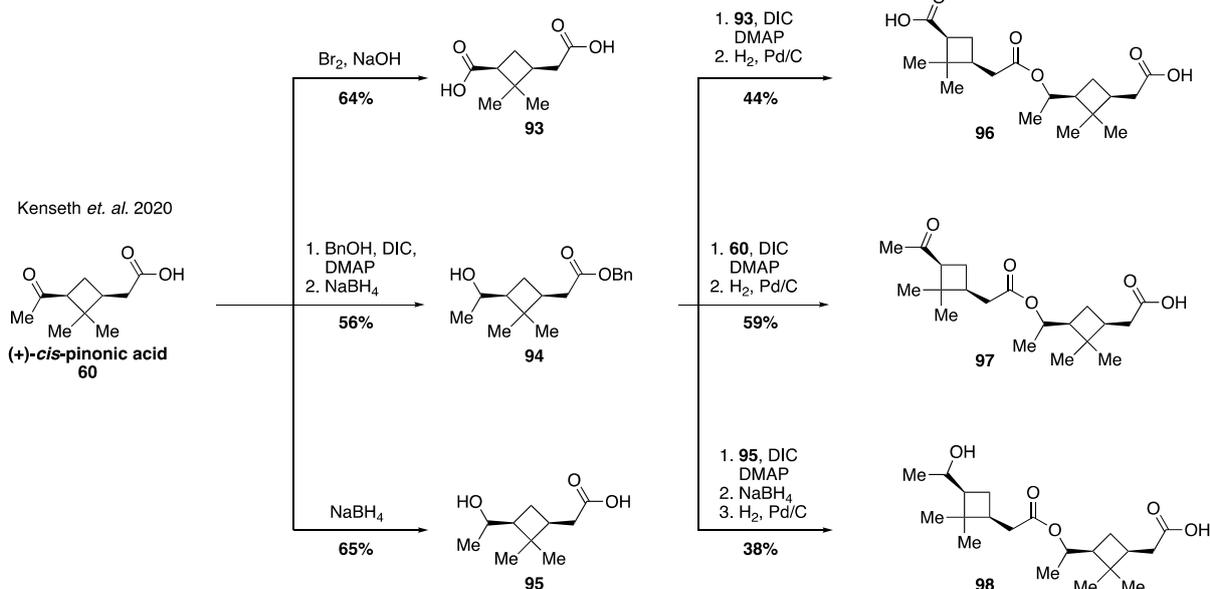


Figure 19. Synthesis of pinene-derived ester dimers as model compounds for mass spectroscopy studies.

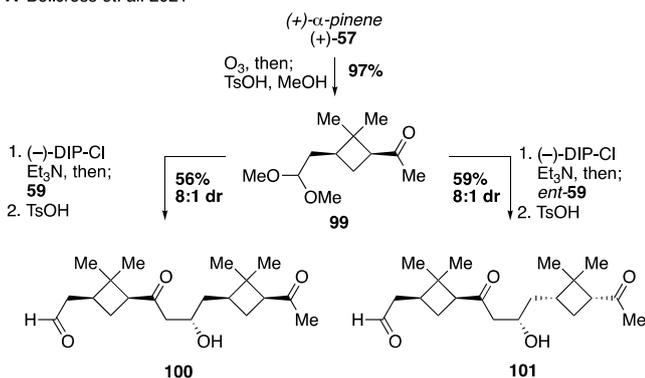
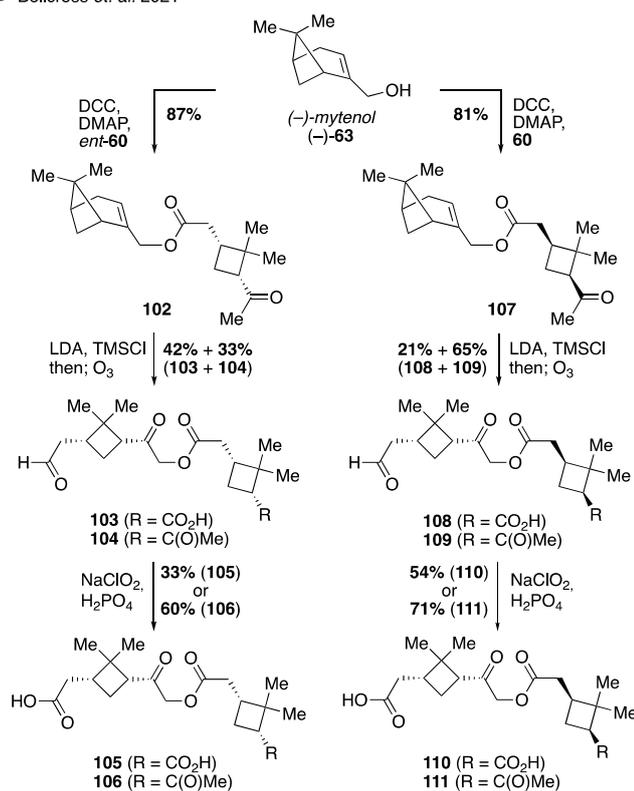
A Bellcross *et. al.* 2021B Bellcross *et. al.* 2021

Figure 20. Synthesis of pinene-derived aldol and ester dimers.

myrtenol (**63**) as a common starting material (Figure 20B). An initial Steglich esterification of **63** with *ent*-pinonic acid (*ent*-**60**) gave ester **102** in 87% yield. The methyl ketone within **102** was converted to its enol silane, and the resultant unpurified compound was exposed to ozonolysis conditions to generate a separable mixture of acid-aldehyde **103** and keto-aldehyde **104** in 42% and 33% yield, respectively. Subsequent oxidation provided the corresponding carboxylic acids, **105** and **106** (from **103** and **104**, respectively). Access to the diastereomeric suite of compounds (i.e., **107–111**) was accomplished using the same sequence of reactions but using the opposite enantiomer of pinonic acid (**60**) in the initial Steglich esterification. With these compounds in hand the authors investigated their ability to depress the surface tension of water droplets, a property linked to cloud formation in the atmosphere. Dynamic surface tension measurements revealed significant difference between

diastereomeric pairs of compounds, indicating that backbone stereochemistry may play an important role in various atmospheric processes and that chirality should be considered more frequently in future models of the climate system.^{212, 213}

4. Sesquiterpene-Derived SOA Material

While isoprene and monoterpenes boast the largest emission rates of biogenic VOCs, sesquiterpenes ($C_{15}H_{24}$) emitted from various coniferous and deciduous plants have been found to have higher reactivity with atmospheric oxidants leading to a potential to form large amounts of aerosols.^{9, 214} The total global sesquiterpene emission is estimated to be ~ 14.8 Tg yr^{-1} , and $\sim 9–16\%$ of total terpene emissions.²¹⁵ In particular, their high reactivity towards O_3 ,^{216, 217} coupled with the very low volatilities of their oxidation products may indicate that SOA formation from sesquiterpenes is currently underestimated.^{218–221} Therefore, aerosol yields from the ozonolysis of sesquiterpenes may be one of the major determinants in the SOA budget in the atmosphere.^{160, 161, 222–224}

A variety of sesquiterpenes have been detected in the atmosphere due to commercially available standards, including β -caryophyllene, α -humulene, longifolene, α -copaene, α -farnesene and α -cedrene.^{215, 225–228} β -Caryophyllene (**112**) is the most abundant sesquiterpene emitted in the atmosphere and is proposed to play an important role in the formation of SOA.^{225, 229–231} Previous studies indicate that low molecular weight compounds form the majority of SOA from the ozonolysis of β -caryophyllene (**112**).^{218, 232–235} While few oxidation products derived from β -caryophyllene (**112**) have been identified, it is the only sesquiterpene for which authentic standards of oxidation products have been synthesized. Due to the availability of these standards there has been accelerated progress in the study of first and second generation oxidation products derived from ozonolysis of β -caryophyllene (**112**) as outlined below.

4.1 Oxidation Products Derived from β -Caryophyllene

Aldehydes derived from β -caryophyllene (**112**) were identified early on in large amounts in both the gas and aerosol phases.^{161, 236} In 2008, authentic standards were synthesized through the ozonolysis of β -caryophyllene with a reductive workup, leading to the formation of β -nocaryophyllene aldehyde (**113**) and β -caryophyllene aldehyde (**114**) (Figure 21A).²²⁹ These standards were used to unambiguously identify and quantify the presence of β -nocaryophyllene aldehyde in field samples from Boreal

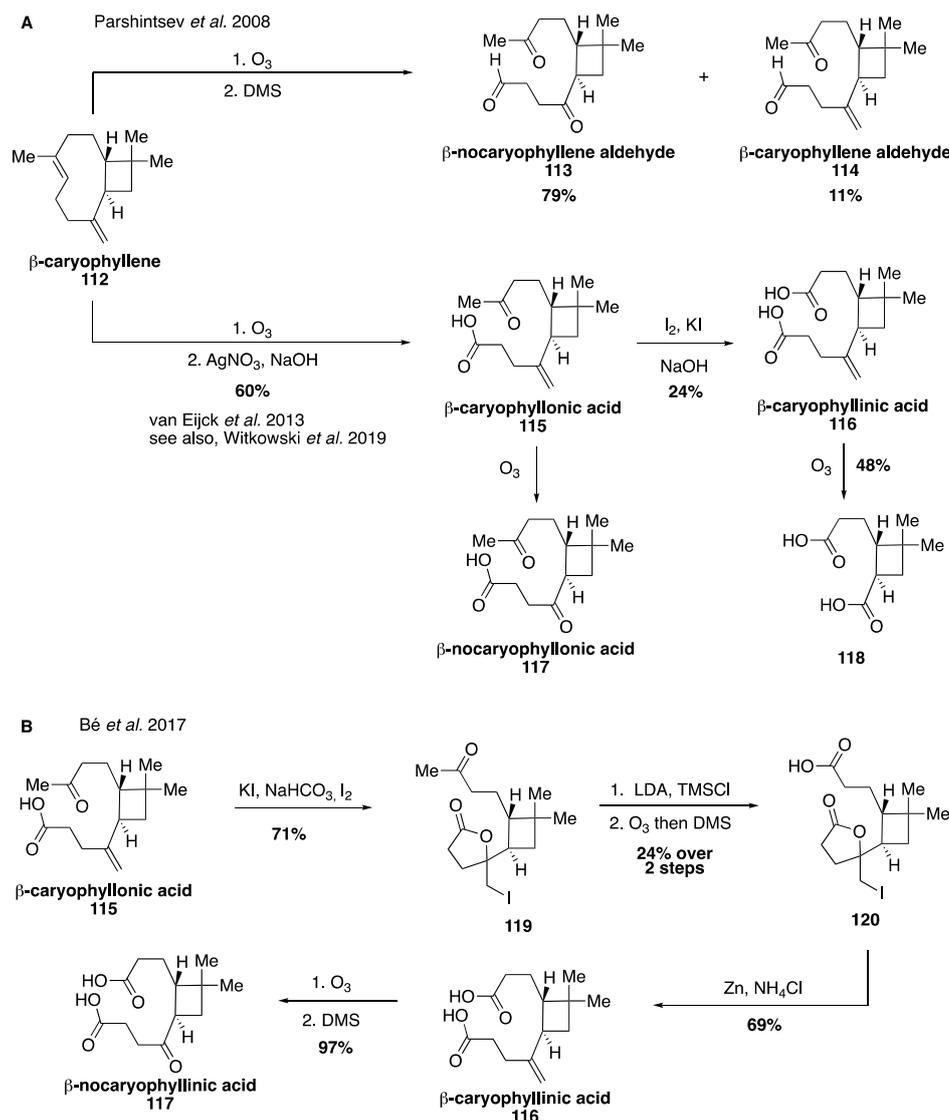


Figure 21. Synthetic routes accessing a number of caryophyllene oxidation products.

forests as well as determine atmospherically relevant properties.^{229, 237} Additional oxidation products derived from β -caryophyllene (**112**) were accessed in 2013, including β -caryophyllonic acid (**115**), β -caryophyllinic acid (**116**) and β -nocaryophyllonic acid (**117**).^{238, 239} While β -caryophyllinic acid (**116**) has been tentatively proposed as an abundant tracer for β -caryophyllene derived SOA,^{222, 240} synthesis of these standards unambiguously identified constituents of β -caryophyllene-derived SOA in both chamber and field experiments and indicated that β -nocaryophyllonic acid (**117**) and β -caryophyllonic acid (**115**) may be important tracers in the particle phase for β -caryophyllene ozonolysis pathways.²³⁸

More recently, β -caryophyllene aldehyde (**113**) and β -caryophyllonic acid (**115**) were identified as highly surface active and therefore may play an important role at the surfaces of β -caryophyllene-derived material, where they would significantly enhance CCN activity (Figure 21B).¹⁵² This study also developed an alternative route to access β -caryophyllinic acid (**116**) and β -nocaryophyllinic acid (**117**) via oxidation of an

iodolactone intermediate (**119**) accessed from β -caryophyllonic acid (**115**).¹⁵²

Many recent studies have proposed a variety of additional tracers for oxidation products derived from β -caryophyllene (**104**) as well as other sesquiterpenes.^{218, 232, 235, 241, 242} Synthesis of additional oxidation products derived from β -caryophyllene and expansion to studies of other sesquiterpenes will be essential for analyzing the impact of sesquiterpenes on SOA formation and accurately quantifying their abundance in the atmosphere.

5. Biogenic SOA Material Influenced by Atmospheric Pollutants

The large numbers of anthropogenic sources around the world result in abundant emissions of primary organic aerosols (POAs) and also influence SOA formation. Processes such as biomass burning and combustion all yield VOCs that can influence the chemistry and composition of SOA particles. Despite the

estimate that biogenic sources for VOCs heavily outweigh anthropogenic sources,² it has been established that SOA formation is greatly enhanced by anthropogenic emissions composed primarily of nitrogen oxides and sulfur dioxide,²⁴³ which can serve as a source of acidic aerosol in the atmosphere.^{9, 10, 244} Many proposed SOA constituents influenced by NO_x or SO_x are highly polar and synthetically challenging to access. As a result, very few synthetic routes have been published to access authentic standards of organosulfate and organonitrate aerosol components. Development of additional synthetic procedures to access these standards would significantly enhance understanding of their chemical composition, atmospheric abundance, as well as chemical and physical properties.

5.1 Organosulfate Species

Organosulfate compounds have recently gained recognition in the atmospheric community as potential markers for SOA particles influenced by acidic sulfate.²⁴⁴⁻²⁴⁷ The main source of sulfate in the atmosphere is oxidation of SO₂ emitted from the combustion of fossil fuels, indicating that detection of organosulfates may also serve as a marker for anthropogenic pollution. Monosulfate esters present in atmospheric aerosols can be produced from acid-catalyzed particle-phase reactions and are generally highly water-soluble, nonvolatile, and negatively charged at acidic pH, such that they remain in the particle phase of aerosols. Organosulfate compounds have been detected in a variety of both laboratory and field studies as a significant component of SOA particles^{246, 248-252} and were observed to form from a variety of precursors such as isoprene, monoterpenes, sesquiterpenes, MBO as well as other aromatic and aliphatic compounds.^{102, 114, 185, 235}

Despite their abundance, until recently only a few organosulfate species have been identified and quantified in the atmosphere since authentic standards of organosulfate products are not commercially available. Several studies have used surrogate standards such as camphorsulfonic acid and galactose sulfate to quantify organosulfates and aerosol material.^{246, 253, 254} Sulfate esters present in organosulfates often have high aqueous solubilities and a propensity to undergo hydrolysis, which can make their isolation and purification challenging. Despite these challenges many of the putative atmospheric organosulfates have been prepared in recent years.

The most abundant and ubiquitous organosulfates are those derived from isoprene.^{35, 39, 102, 246, 255} The organosulfate derived from IEPOX and 2-methyltetraol oxidation products (m/z 215) was identified as one of the most abundant single organic compounds in atmospheric aerosols.^{32, 33, 256} An NMR spectrum for a mixture of IEPOX-derived organosulfate isomers as tetrabutylammonium salts has been published⁵⁹ and this mixture has been used as a standard in several field studies.^{59, 70, 257} More recently, one of the four possible IEPOX-derived organosulfate regioisomers (**121**) was synthesized under Bu₄NHSO₄ conditions from epoxide **5** (**Figure 22**),²⁵⁸ yet the development of synthetic routes to access all regio- and

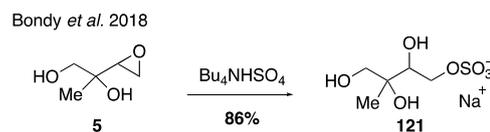
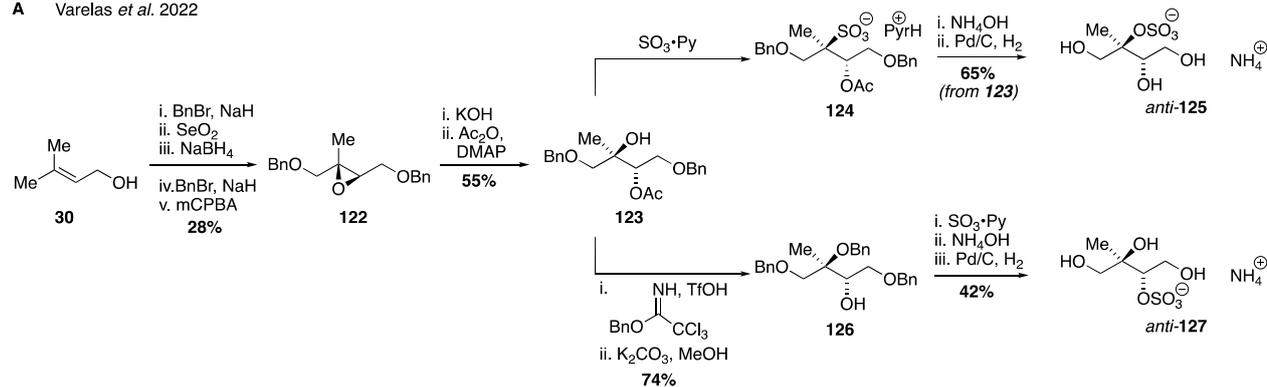
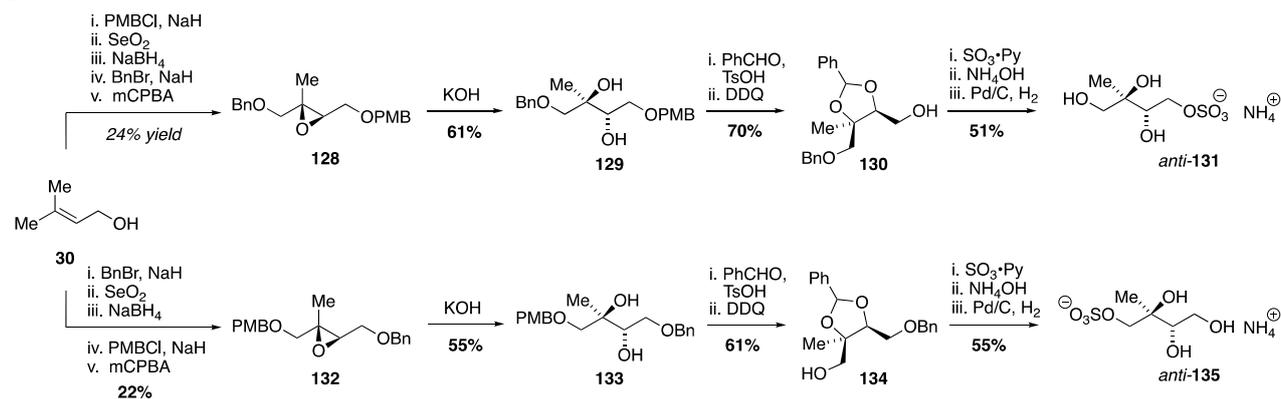
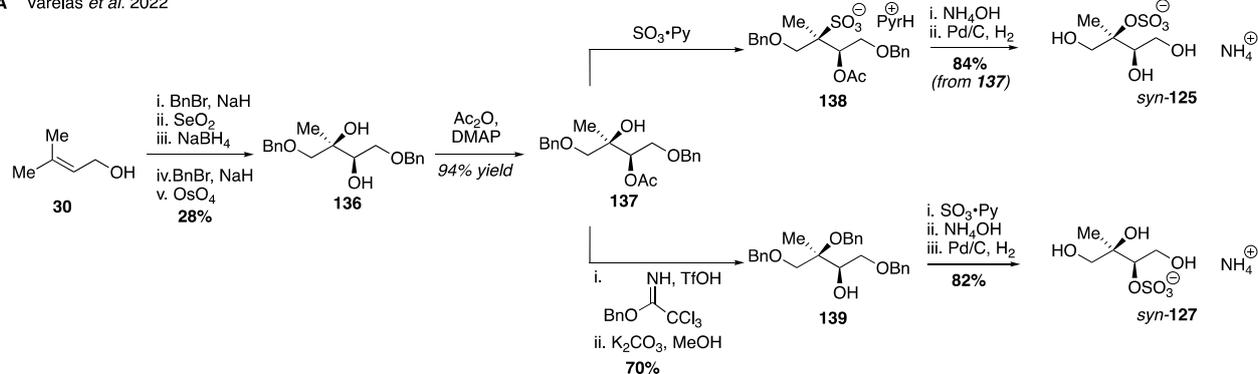
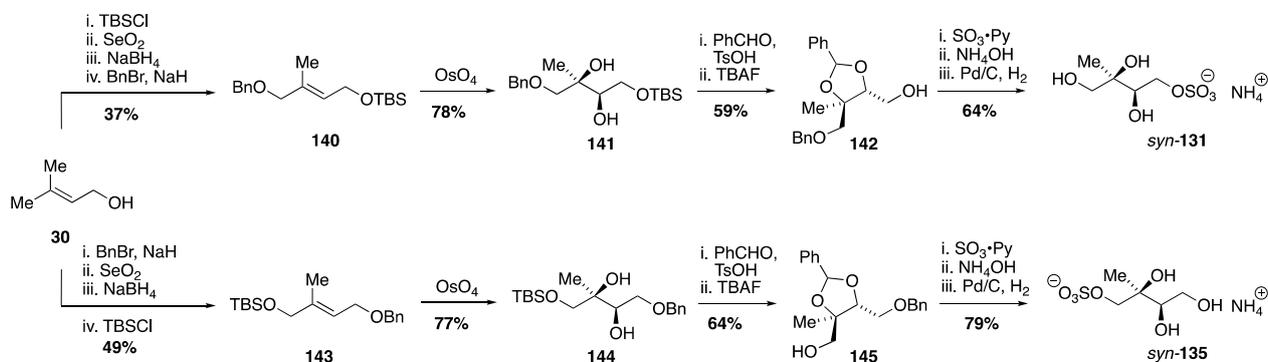


Figure 22. Sulfation through epoxide opening.

stereoisomers of the IEPOX-derived organosulfates has been challenging.

Since primary, secondary and tertiary isomers (as well as syn and anti stereoisomers) may have different rates of hydrolysis and therefore atmospheric lifetimes and properties,^{81, 259} access to atmospherically relevant salts of each IEPOX-derived sulfate isomer is desirable.²⁵⁷ Isolation of pure isomers will also aid in quantifying the relative amounts of these isomers in the atmosphere and provide insight into the aging and fate of SOA influenced by anthropogenic emissions. Recent work from our own labs has established detailed synthetic routes that have enabled access to all eight possible regio- and stereoisomers of the IEPOX-derived organosulfate isomers as racemates. Access to the *anti*-configured sulfate regioisomers (corresponding to threitol stereochemistry) was accomplished using prenol **30** as a common starting material (**Figure 23A**). The tertiary and secondary sulfates *anti*-**125** and *anti*-**127**, respectively, were prepared from protected tetraol **123** as a point of divergence, with the desired stereochemical configuration arising from the stereoselective basic hydrolysis of epoxide **122**. Direct sulfation of tertiary alcohol **123** was accomplished using sulfur trioxide pyridine complex to afford sulfate ester **124**, which was further processed to the desired tertiary sulfate *anti*-**125** by counter ion exchange and global protecting group removal by hydrogenolysis. Alternatively, the secondary organosulfate *anti*-**127** could be synthesized from protected tetraol **123** via benzyl ether **126**. Sulfation of the free secondary alcohol within **126** followed by sulfation and protecting group removal delivered the desired compound in an efficient fashion. The two primary organosulfate isomers, *anti*-**131** and *anti*-**135**, were also generated using prenol **30** as the starting material (**Figure 23B**). Differentiation of the two primary hydroxyl groups was accomplished early in each route through the selective introduction of benzyl or *para*-methoxybenzyl ether groups on either of the terminal alcohols, allowing the isomeric epoxides, **128** and **132** to be prepared. Epoxide opening followed by a series of protecting group manipulations and sulfate installation analogous to the secondary and tertiary sulfate synthesis, then provided the two primary organosulfates, *anti*-**131** and *anti*-**135**.

In an analogous series of reactions that also used prenol **30** as the starting material, the series of *syn*-configured sulfate regioisomers (corresponding to the erythritol stereochemistry) was also prepared (**Figure 24**). The key difference between the approach used to access these diastereomeric compounds was the method employed to introduce the secondary and tertiary hydroxyl groups: while the *anti*-stereochemistry was generated through epoxidation followed by hydrolytic ring-opening, the *syn*-stereochemistry was obtained by stereospecific osmium-catalyzed dihydroxylation. In this way, diols **136**, **141** and **144**

A Varelas *et al.* 2022B Varelas *et al.* 2022Figure 23. Diastereoselective synthesis *anti*-configured IEPOX-derived organosulfate isomers.A Varelas *et al.* 2022B Varelas *et al.* 2022Figure 24. Diastereoselective synthesis *syn*-configured IEPOX-derived organosulfate isomers.

were forged and then manipulated to produce each of the requisite *syn*-sulfates using a series of protecting groups similar to those employed in the *anti*-sulfate series. Access to this complete set of all eight isomers in diastereomeric form allowed for a series of investigations into their stability and acidity properties. The tertiary sulfates were shown to be the least stable in aqueous solution with half-lives of 4.5 days, while the secondary and primary sulfates were stable for greater than 60 and 180 days, respectively. Interestingly, the pKa of the tertiary sulfates were reported to be lower than the secondary and primary isomers (ca. 3 for **125**, 4 for **127** and 5 for **131/135**), although at this stage no rational explanation for these differences has been provided. Ultimately, while the synthetic chemistry required to access each of these isomers was somewhat laborious this careful approach led to some important new insights and lays the foundation for future studies on pure samples, such as investigating their role in gas particle uptake and hygroscopic growth.²⁶⁰

Glycolic acid sulfate (**147**) was first synthesized and identified in 2009, which confirmed its previous misidentification in field and chamber studies as glyoxal sulfate.²⁶¹ Glycolic acid sulfate (**147**) and its structurally related lactic acid sulfate (**149**) were synthesized from glycolic acid (**146**) and lactic acid (**148**), respectively, using diisopropylethylamine (DIEA) and chlorosulfonic acid (Figure 25).²⁶¹ Access to these standards allowed for studies to determine that they are ubiquitously detected in a variety of locations but only account for less than 0.2% of organic aerosols in those areas.^{262, 263} Glycolic acid sulfate (**147**) was later synthesized as the potassium salt from **146** using a pyridine sulfur trioxide complex. A hydroxyacetone sulfate (**151**) and benzyl sulfate were accessed using the same procedure from hydroxyacetone (**150**) and benzyl alcohol.²⁶³ Their syntheses allowed for their quantification in aerosol samples and the advancement of hydrophilic interaction liquid chromatography coupled with mass spectrometry, which provides excellent separation of isoprene-derived carboxy-organosulfates.²⁶³⁻²⁶⁵ Synthesis of additional dihydroxybutanone and dihydroxybutanal organosulfate isomers (**154**, **155**, **158**, **159**) also led to identification of the sulfate isomers of 3,4-dihydroxybutan-2-one (**158** and **159**) in atmospheric aerosols (Figure 26).⁴⁴

Organosulfates derived from monoterpenes, such as α -pinene, β -pinene, and limonene, have also been detected in field and chamber aerosol studies around the world.^{103, 156, 245, 254, 266-268} Epoxides containing tertiary carbons have been shown to react quickly with acidic sulfate sources,²⁶⁹ indicating that compounds such as β -pinene oxide (**160**) may react readily to form organosulfates.²⁷⁰ In order to investigate formation of organosulfates from monoterpenes, a mixture of β -pinene organosulfates (2-pinanol-10-hydrogensulfate and 10-pinanol-2-hydrogensulfate, **161** and **162**) were synthesized via the addition of sulfuric acid to **160** (Figure 27).¹⁸⁵ These standards were used to demonstrate that β -pinene organosulfates may be present in concentrations up to 23 ng m⁻³ ambient SOA, however it is possible that the structural assignments of **161** and

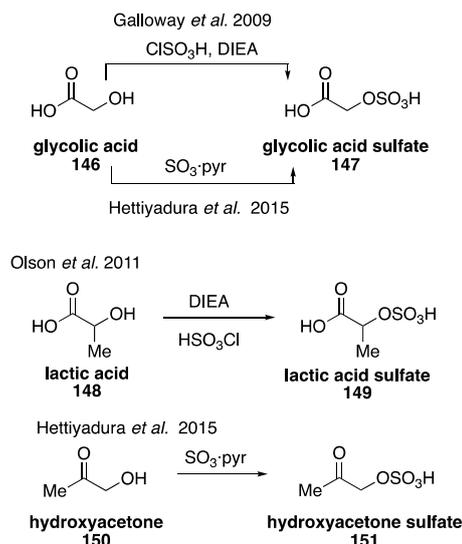


Figure 25. Synthesis of sulfates derived from glycolic acid, lactic acid and hydroxyacetone.

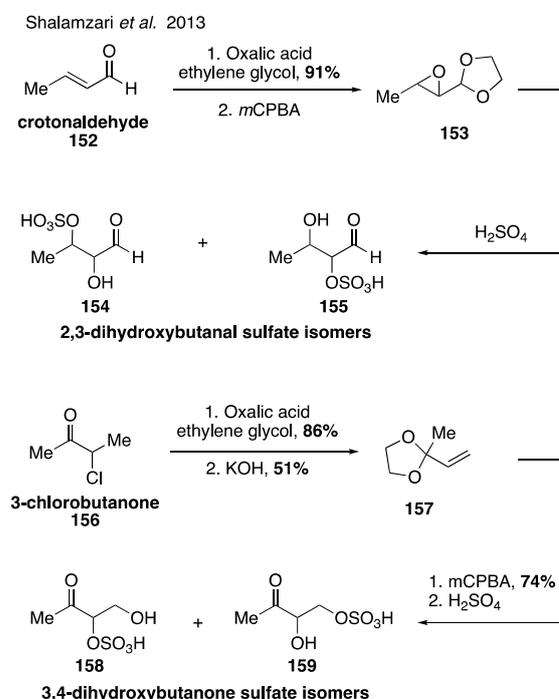


Figure 26. Synthesis of sulfated butanal and butanone species.

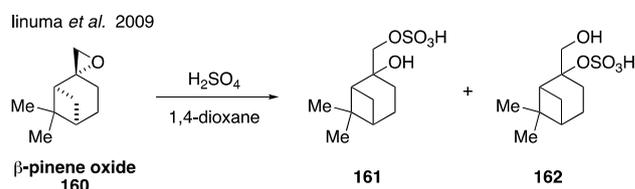


Figure 27. Synthesis of pinene-derived organosulfates.

162 are incorrect given the propensity for β -pinene oxide to undergo acid catalyzed rearrangement. Detailed structural assignment using NMR spectroscopy was not reported. Limonene-derived organosulfates were recently synthesized²⁷¹ by treating a mixture of limonene oxides (**163** and **164**) with

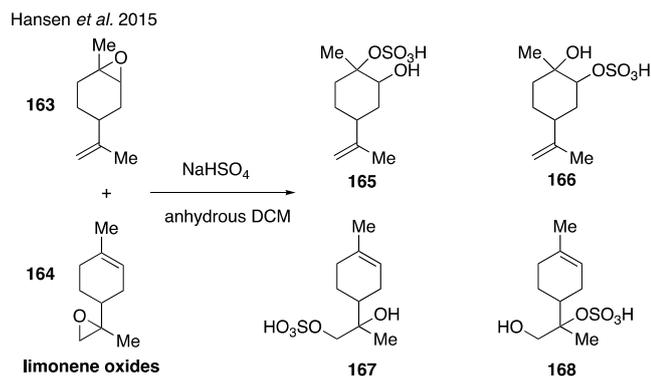


Figure 28. Synthesis of limonene-derived organosulfates.

sodium bisulfate following synthetic protocols developed by Cavdar and coworkers (Figure 28).²⁷² While the limonene-derived organosulfates (165–168) were unable to be separated and contained other organosulfate impurities, the surface activity and hygroscopicity of the resulting mixture were analyzed in order to further understand the atmospheric impact of organosulfates derived from monoterpenes.²⁷¹

In 2017, Wang and coworkers reported a strategy for the synthesis of monoterpene-derived organosulfates via diastereoselective dihydroxylation followed by monosulfation with sulfur trioxide-pyridine complex (Figure 29).²⁷³ Upjohn dihydroxylation of α -pinene and β -pinene with catalytic osmium tetroxide and stoichiometric NMO provided the corresponding diols **58** and **171** as single diastereomers due to steric hindrance from the bridged *gem*-dimethyl groups. However, when limonene (**173**) was subjected to the same conditions, a mixture of diastereomers was obtained due to lack of steric differentiation. This problem was addressed by employing Sharpless asymmetric dihydroxylation using AD-mix- β , which provided major diastereomer **174** in 20:1 dr. The diols were subsequently treated with sulfur trioxide-pyridine complex to provide the corresponding organosulfate standards (i.e., **169**, **172** and **175**), with the sulfate group installed at the less sterically hindered position. With authentic standards in hand, the authors discovered that β -pinene derived organosulfate **172** degrades to a dehydrogenated organosulfate compound and a hydroperoxyl organosulfate compound over prolonged storage. In addition, the authors were the first to report identification of limonene and limonaketone organosulfates in ambient samples collected in the Pearl River Delta, China.²⁷³

Wang and coworkers expanded on this work in their groundbreaking 2019 study, generalizing their two-step dihydroxylation/sulfation route to eight monoterpenes (i.e., α - and β -pinene, limonene, sabinene, Δ^3 -carene, terpinolene, and α - and γ -terpinene) and two sesquiterpenes (i.e., α -humulene and β -caryophyllene) to synthesize a total of 26 α -hydroxy organosulfate standards, of which major isomers were isolated (Figure 30) and the minor isomers were analyzed via LC/MS and MS/MS.²⁷⁴ Retention times and MS/MS characteristics of the synthesized standards subsequently enabled the detection of α -hydroxy organosulfates derived from Δ^3 -carene, sabinene, terpinolene, and β -caryophyllene in ambient samples for the

first time.²⁷⁴ An additional outcome of this work were new potential insights into the formation mechanisms of organosulfates in the atmosphere and the importance of whether sulfation occurs from acidic opening of an epoxide or by direct sulfation of an alcohol. Epoxide precursors typically yield rearranged organosulfate products, while diol precursors allow the formation of products with the cyclobutane intact. Further work in this important area will likely rely on extensive use of synthetic standards.

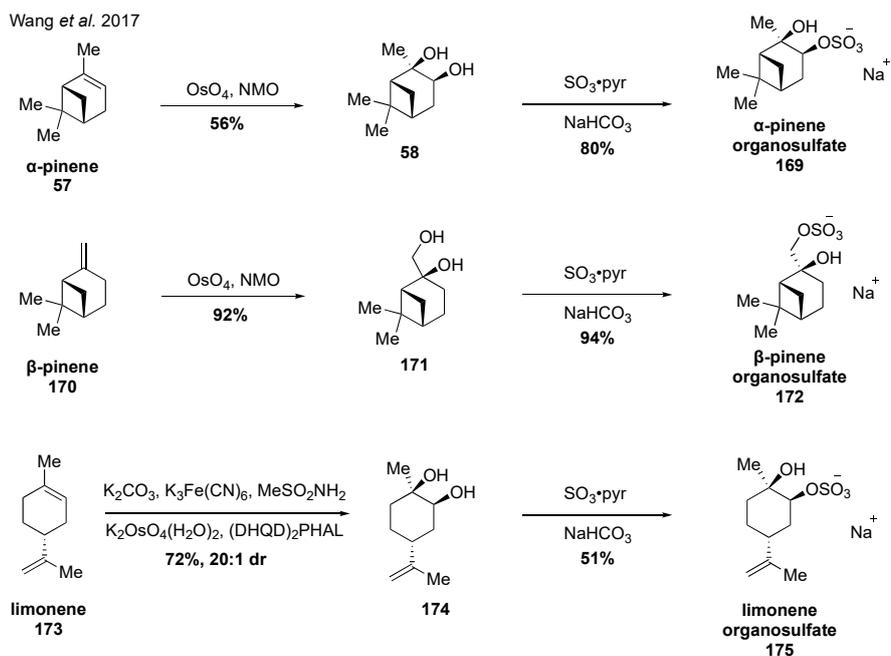


Figure 29. Access to complex organosulfate species through diastereoselective dihydroxylation followed by regioselective sulfation.

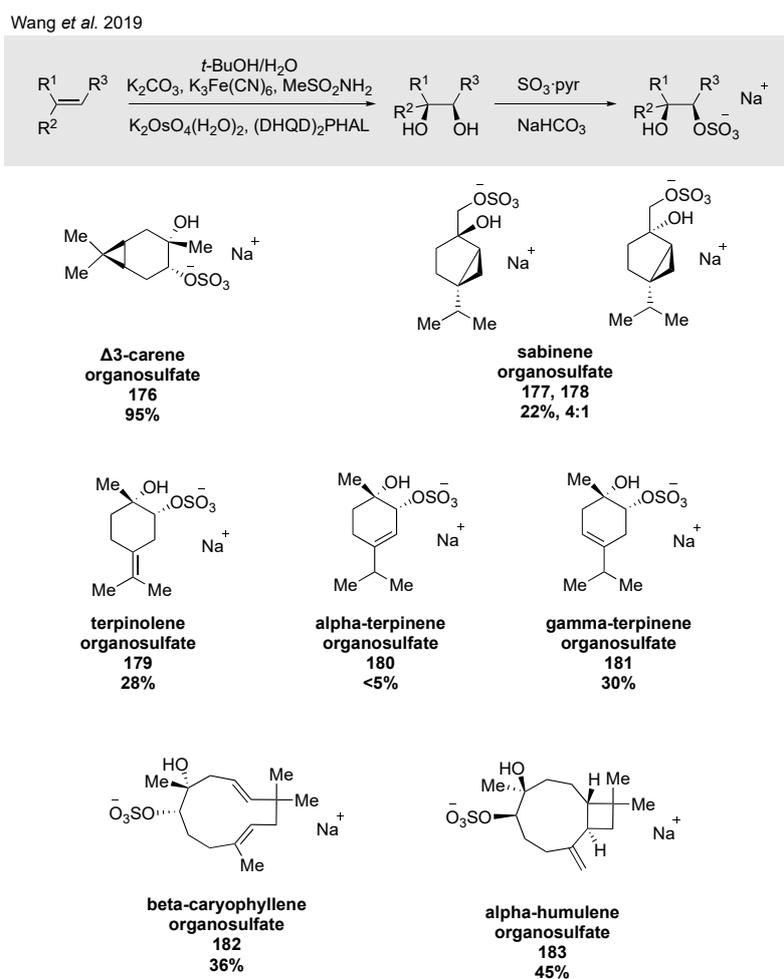


Figure 30. A general protocol for the diastereo- and regioselective installation of sulfate esters across alkenes.

5.2 Organonitrate Species

Nitrogen oxides (NO_x) are predominantly emitted from combustion of fossil fuels and change the oxidation pathways of VOCs through the formation of organonitrates.²⁷⁵⁻²⁷⁷ In high NO_x environments, nitric oxide can add to peroxy radicals in the atmosphere to form organonitrate compounds. The nitrate radical (NO_3) serves as a strong oxidant in the nighttime atmosphere (since it undergoes rapid photolysis in sunlight) and has been shown to react quickly with unsaturated BVOCs.²⁷⁸⁻²⁸⁰

Organonitrates are often stable but can also hydrolyze readily in the particle phase, especially at tertiary positions and at high humidities, to form nitric acid.^{259, 281-284} While this reaction is likely acid-catalyzed, its mechanism remains uncertain.^{81, 285} The effect of organonitrates on atmospheric nitrogen levels and secondary organic aerosol has therefore been the topic of a variety of studies.^{30, 286-288} However, due to a current lack of authentic standards, elucidation of information related for mechanisms of oxidation at high NO_x concentrations and identification of organonitrate species remains challenging, making their synthesis a priority for future studies.²⁸⁹

The synthesis of organonitrates has been achieved through nitration of alkyl halides with silver nitrate, nitration of alcohols or alkanes using nitric acid,²⁹⁰⁻²⁹³ or treatment of alcohols with dinitrogen pentoxide.²⁹⁴ More recently hydroxyl nitrate esters have been accessed through epoxide opening in the presence of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.²⁹⁵⁻²⁹⁷ Multifunctional nitrates have also been accessed²⁹⁸⁻³⁰¹ and carbonyl containing nitrate compounds have been synthesized through the nitration of hydroxy ketones with dinitrogen pentoxide.^{294, 302} Many of these syntheses have resulted in the isolation of a mixture of products, indicating that additional work is needed to isolate pure authentic standards. These initial studies have established several physical properties of small molecule organonitrates and may prove useful in future attempts to access atmospheric standards, since multifunctional organonitrates (possessing four or more oxygen atoms) dominate nitrate mass in submicron particles.³⁰³

Organonitrates formed from isoprene under high NO_x conditions have been detected in the gas phase and can partition to the particle phase due to their low volatilities, while under low NO_x conditions in pristine environments organonitrates are expected to have negligible yields.³⁰⁴⁻³⁰⁷ Isoprene-derived hydroxynitrates are some of the few standards that have been synthesized and analyzed in atmospheric studies.^{298, 300, 301} Four of the eight possible isoprene hydroxyl nitrate isomers (2-methyl-1-nitrooxybut-3-ene-2-ol (β -2,1 **184**), 2-methyl-2-nitrooxybut-3-ene-1-ol (β -1,2 **185**), 2-methyl-4-nitrooxybut-2-ene-1-ol (δ -1,4 **186** and **187**), **Figure 31**) were synthesized in 2010 via the addition of nitric acid to 2-methyl-2-vinyl oxirane (**17**).³⁰⁸ While the original synthesis did not allow for the separation of the *cis* and *trans* isomers of the δ -1,4 nitrate (**186**, **187**), this was later achieved in the synthesis of both the *cis* and *trans* δ -1,4 nitrate (**186**, **187**) as well as the additional synthesis of another isomer, 3-methyl-2-nitrooxybut-3-ene-1-ol (β -4,3 **188**) via the ring-opening reaction of the corresponding epoxide precursor with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (**Figure 32**).³⁰⁹

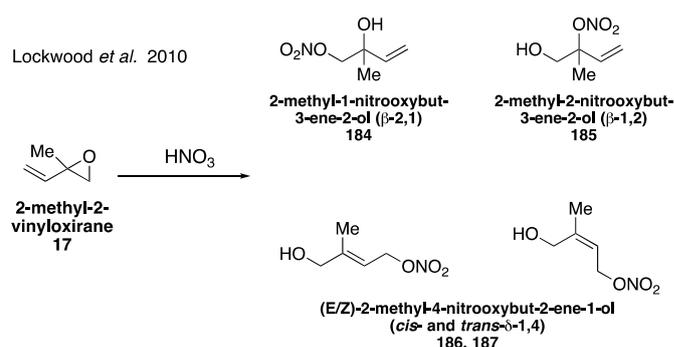


Figure 31. Unselective synthesis of isoprene-derived organonitrates using nitric acid.

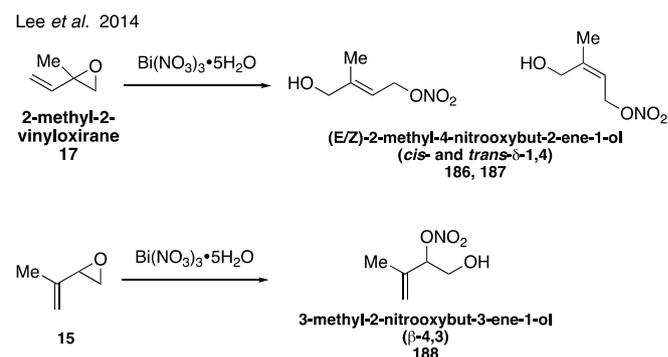


Figure 32. Improved selectivity for organonitrate synthesis using bismuth nitrate.

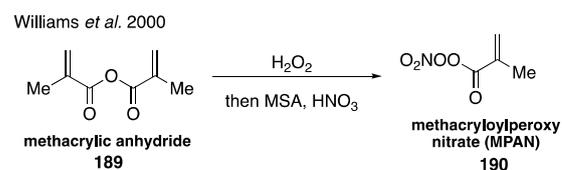


Figure 33. Synthesis of MPAN.

Synthesis of these authentic standards demonstrated the relative importance of the individual isoprene nitrate isomers as well as their different reactivities with atmospheric oxidants.^{308, 309} Since these isoprene nitrates retain a degree of unsaturation, they are highly reactive and can produce higher order organonitrate products proposed in the literature.^{289, 309} For instance, chamber studies have identified methacryloylperoxynitrate (MPAN, **190**) as a second-generation product.^{32, 33} The synthesis of MPAN from the peroxidation of methacrylic anhydride (**189**) followed by nitration³¹⁰ confirmed that acyl peroxynitrates play an important role in SOA formation under high NO_x conditions (**Figure 33**).^{33, 108}

Recently, Nguyen and coworkers expanded the current library of isoprene-derived hydroxynitrate standards with the synthesis of 2-methyl-3-nitrooxybutane-1,2,4-triol (**193**) and 2-methyl-1,4-dinitrooxybutane-2,3-diol (**198**) from isoprene (**1**) (**Figure 34**).³¹¹ The synthesis of both **193** and **198** began with

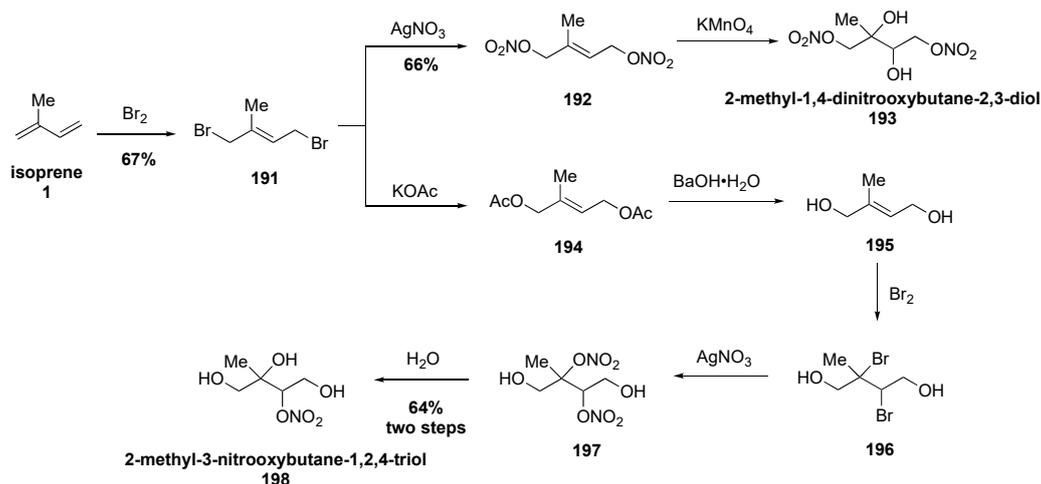


Figure 34. Synthetic route for accessing complex organonitrates derived from isoprene.

the direct bromination of isoprene (**1**) to yield dibromoalkene **191**. Direct nitration of bromide **191** with AgNO_3 followed by dihydroxylation with KMnO_4 gave **193**. To access compound **198** dibromide **191** was treated with potassium acetate followed by hydrolysis and bromination to obtain dihydroxy dibromide compound **196**. Subsequent nitration with AgNO_3 afforded the unstable dinitrate **197** which spontaneously hydrolyzed to **198**. These new organonitrate standards were used along with previously synthesized organosulfate standards to study their OH-initiated oxidation kinetic rate coefficients, leading the authors to conclude that aqueous photooxidation of isoprene-derived SOA compounds may affect the SOA budget when incorporated into global models.³¹¹

NO_x initiated oxidation of monoterpenes can compete with ozonolysis in the atmosphere to result in SOA formation.³¹²⁻³¹⁴ Monoterpene-derived organonitrates may represent a significant fraction of SOA.^{315, 316} Organonitrate **199** derived from α -pinene was synthesized starting from α -pinene oxide (**70**) in the presence of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Figure 35).³¹⁷ Along with rate constant data, product identification confirmed that a unimolecular specific acid-catalyzed mechanism is responsible for hydrolysis of the α -pinene derived organonitrate under acidic conditions.³¹⁷

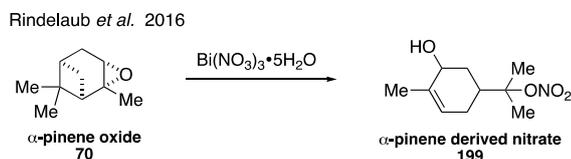


Figure 35. Synthesis of a pinene-derived organonitrate.

In 2020, McKnight and coworkers expanded this method to synthesize nine organonitrates derived from monoterpenes (Figure 36) including Δ^3 -carene, limonene, α -pinene, β -pinene and perillalcohol.³¹⁸ Exposing α -pinene oxide and β -pinene oxide to $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ both resulted in multiple carbocation rearrangement products.³¹⁸ A 2021 study by Wang and coworkers reported the regioselective synthesis of several terpene-derived organonitrates.³¹⁹ Access to these species was accomplished via two routes: epoxidation of the terpene to

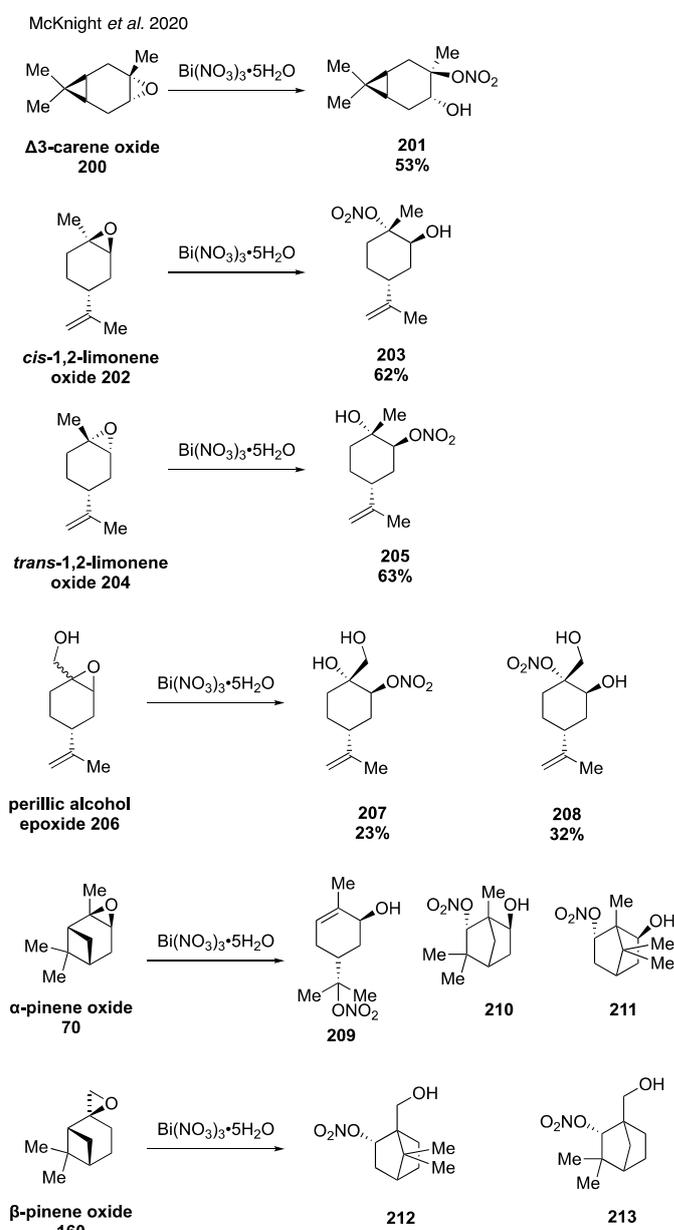


Figure 36. Diverse organonitrates accessed using bismuth nitrate.

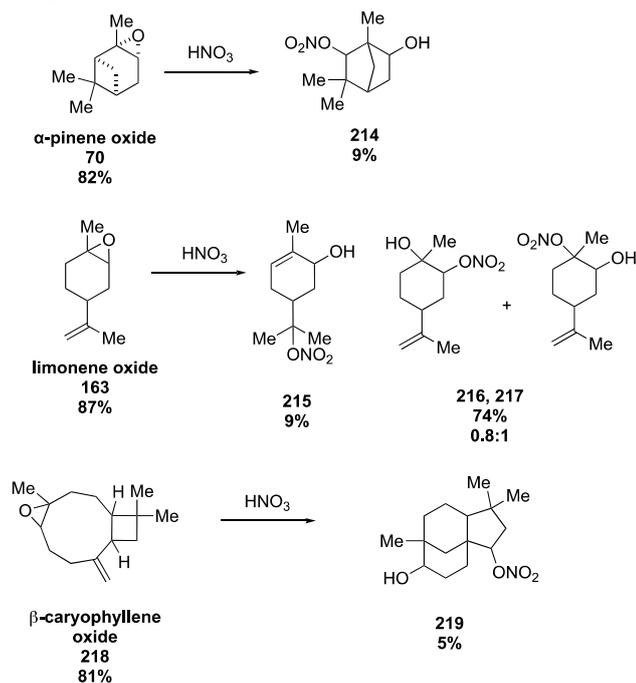
Wang *et al.* 2021

Figure 37. Organonitrates derived from epoxide opening with nitric acid.

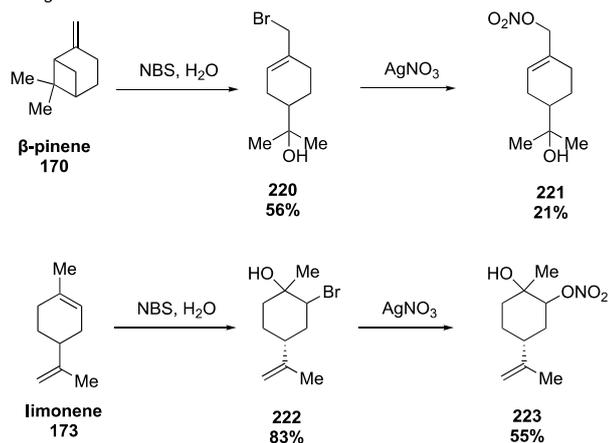
wang *et al.* 2021

Figure 38. Organonitrate from halides by displacement with silver nitrate.

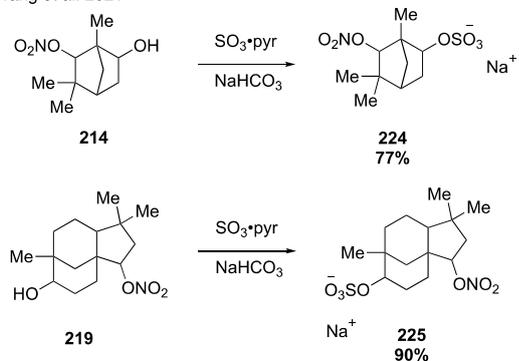
Wang *et al.* 2021

Figure 39. Complex nitroxy organosulfates.

deliver an epoxide that was opened with concentrated nitric acid (**Figure 37**) or regioselective bromohydration of the terpene with NBS followed by nitration with AgNO_3 (**Figure 38**). Two of the synthesized organonitrates, β -pinene derived organonitrate **221** and β -caryophyllene derived organonitrate **219**, had not been previously reported. The same synthesis methods were used in a later study to further investigate the hydrolysis mechanism of terpene-derived organonitrates. Consistent with Rindelaub's findings in 2016,³¹⁷ tertiary and secondary organonitrates were found to hydrolyze via a unimolecular acid-catalyzed mechanism.³²⁰ Primary organonitrates were found to hydrolyze via competing unimolecular and bimolecular mechanisms.³²⁰

In addition, Wang and coworkers demonstrated the feasibility of sulfating complex organonitrate species using sulfur trioxide (**Figure 39**).³¹⁹ Several of the resulting nitroxy organosulfates were then identified in ambient aerosol samples for the first time, correcting previous misidentifications and confirming the existence of previously unrecognized rearrangement pathways in the atmosphere.³²⁰

6. Synthesis of Mechanistic Probes

6.1 Synthesis of Isotopically-labelled Species

The synthesis and use of isotopologues derived from BVOCs holds the promise of enabling detailed molecular studies of biogenic SOA particle chemistry and physics. Recently, synthetic strategies to access isotopically-labeled oxidation products of BVOCs, namely α -pinene, have been developed to aid in studying the composition and formation chemistry of SOA particles as well as chemical exchange between particles.^{321, 322} Synthetic access to the isotopologues of α -pinene coupled with the ability to synthesize laboratory-derived SOA material has also opened up new approaches for studying SOA material using vibrational spectroscopy^{323, 324} and mass spectrometry.³²⁵ In 2016, Upshur and coworkers developed protocols for accessing pinene isotopologues containing deuterium at the C10 vinyl methyl group and the C9 endo disposed methyl group (**Figure 40**).³²³ The routes rely on nopinone (**226**) as a common intermediate, which can be converted to the vinyl isotopologue **227** by a straightforward addition of the CD_3 -cuprate to the corresponding enol triflate in 57% yield. On the other hand, addition of methyllithium to nopinone (**226**) allowed for the generation of caged ether **228** by means of a Suarez functionalization. Opening of the ether bond led to the C9 alcohol **230** which was oxidized to the corresponding carboxylic acid **234** with PDC. Reduction of **234** with LiAlD_4 produced deuterated alcohol **236**, which was further transformed to the desired C9 deuterated methyl analog **240** by LiAlD_4 displacement of the corresponding tosylate **238**. The route was sufficiently flexible to enable access to other isotopologues with varying degrees of deuterium incorporation at C9 and C10 (i.e., **233**, **241** and **242**).

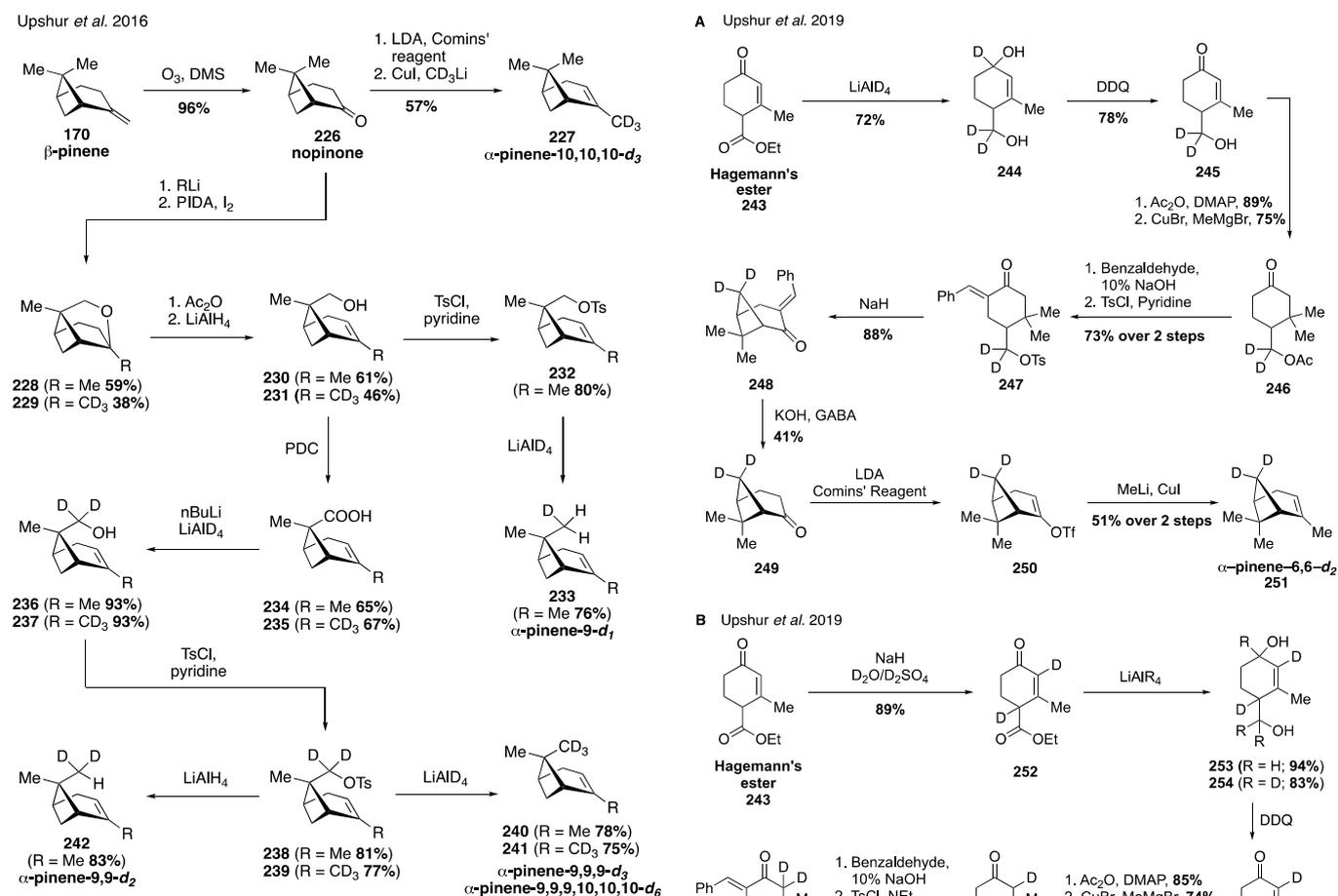


Figure 40. Access to deuterated isotopologues using nopinone as a starting material.

To gain further access to a wider range of pinene isotopologues, such as those with methylene bridge, bridgehead methine, allylic, and vinyl deuteration the same group devised a strategy for the *de novo* synthesis of α -pinene isotopologues adapted from a previous total synthesis completed by Thomas and Fallis (Figure 41).^{326, 327} The syntheses of α -pinene-6,6-*d*₂ (Figure 41A) and α -pinene-1,3,4,4,5,5-*d*₅ and α -pinene-1,3,4,4,5,6,6-*d*₇ (Figure 41B) all utilize a bottom-up approach starting from Hagemann's ester (243), allowing for the generation of multiple site-specifically labeled analogues in a unified fashion.³²⁴ For the case of α -pinene-*d*₂ (251), introduction of the desired deuterium atoms took place in the first step of the synthesis with the LiAlD₄ reduction of Hagemann's ester (243) to deliver diol 244 (Figure 41A). Oxidation with DDQ then gave enone 245 which was converted through a series of steps to tosylate 247, which underwent intramolecular cyclization to afford the key cyclobutene ring as was shown by Thomas and Fallis in their pioneering pinene synthesis. Cleavage of the benzylidene group then allowed for the final formation of the alkene using the cuprate procedure devised in the earlier synthesis of isotopologues (see Figure 40). By modifying this route to include an additional deuteration of Hagemann's ester (243) to form bis-deuterated species 257, the authors were able to access several other highly deuterated compounds (i.e., 265 and 256) in an effective fashion highlighting the generality of the approach (Figure 41B).

Figure 41. Total synthesis of pinene isotopologues from Hagemann's ester.

By subsequently preparing and collecting surface vibrational spectra of SOA material derived from the α -pinene isotopologues, initial attempts were made toward identifying the surface oscillators in α -pinene-derived SOA particles.³²⁴ These α -pinene isotopologues have also been used in mechanistic chamber-based studies, including the demonstration of particle-particle chemical exchange using single-particle mass spectrometry.³²¹ Specifically, SOA mixing experiments using these isotopologues revealed that there is little limitation to diffusion among SOA particles derived from unlabeled and deuterated α -pinene SOA, however, diffusion and uptake of semi-volatile compounds is limited when deuterated α -pinene SOA is mixed with SOA derived from other BVOCs such as limonene and β -caryophyllene.³²¹ Additionally, work aiming to identify intramolecular hydrogen migration in

autoxidation leading to highly oxygenated multifunctional organic compounds has utilized isotopologue **227**.³²⁵ The distribution patterns of SOA products generated from ozonolysis and OH-oxidation of unlabeled α -pinene and isotopologue **227** revealed a systematic shift in the mass of monomers in the deuterated system that was explained by the decomposition of isomeric vinylhydroperoxides to release vinyloxy radical isotopologues, which serve as precursors to a sequence of autoxidation reactions that ultimately yield ELVOCs contributing to SOA formation and growth.³²⁵ These studies would not have been possible without access to isotopically labeled analogues, given that mass spectra of SOA populations generated from different terpenes cannot be differentiated otherwise.

While current synthetic efforts are primarily dedicated to deuterium labeling of α -pinene, a limited number of studies have focused on isotopic labeling of other SOA precursors and

oxidation products. *Trans*- β -IEPOX-*d*₂ (**270**) was synthesized from aldehyde **267** in a four-step route involving a Corey–Gilman–Ganem oxidation, deuterium-installation via reduction, epoxidation, and TBS deprotection (**Figure 42**).^{328, 329} Deuterated analogues **275** and **277** derived from β -caryophyllene, along with other sesquiterpenes (i.e. aromadendrene and isolekene), were prepared in 2016 via synthetic routes hinging on the use of Wittig olefination and α -hydrogen–deuterium exchange (**Figure 43**).³³⁰ Beyond deuterium incorporation, ¹³C-labeled β -pinene (**278**) was recently synthesized from ¹³C-iodomethane and nopinone (**226**) using Wittig olefination chemistry to aid in investigating O₃- and OH-initiated oxidation of β -pinene (**Figure 44**).³²² Further studies focused on the synthesis of BVOC and oxidation product isotopologues, along with the generation of particles derived from such molecules, will bring the field steps closer to elucidating properties and formation mechanisms of biogenic SOA particles.

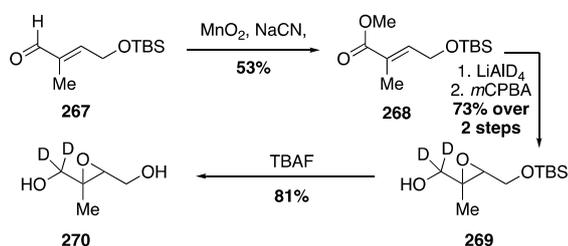
Chase *et al.* 2015

Figure 42. Synthesis of deuterium labelled IEPOX.

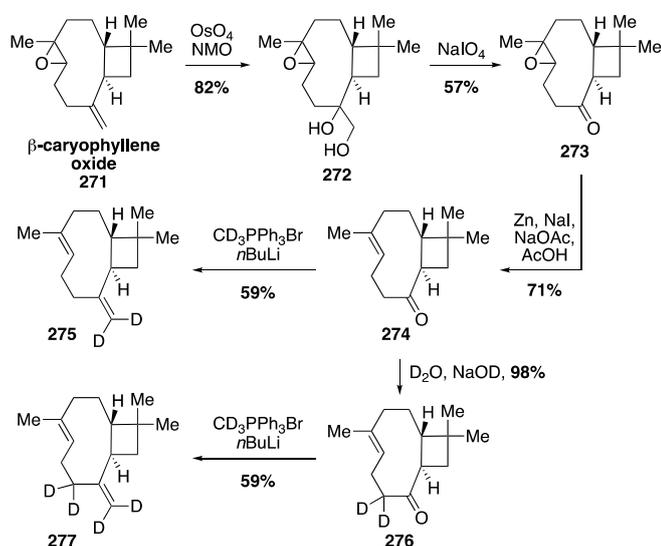
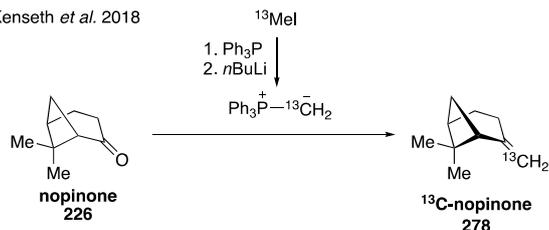
Duhamel *et al.* 2016

Figure 43. Preparation of deuterated caryophyllene species.

Kenseth *et al.* 2018Figure 44. Direct access to ¹³C-labeled pinene through a Wittig reaction.

6.1 Miscellaneous Probe Compounds

A recent publication from the Zhang lab reported the synthesis of two unsaturated analogs of pinonaldehyde (i.e., **279** and **281**) in order to gain new insights into the breakdown of Criegee intermediates formed during the ozonolysis of α -pinene in the atmosphere (**Figure 45**).³³¹ A selective methylenation of the more reactive aldehyde group within pinonaldehyde (**59**) allowed for a direct synthesis of analog **279**, while a slightly more circuitous route involving a protecting group was required to deliver analog **281**. Ozonolysis of each of these species then allowed for detailed studies into the different pathways for SOA formation from the two regioisomeric Criegee intermediates. Future synthetic work along these lines and in concert with computational modeling could reveal important new levels of understanding of these complex processes.

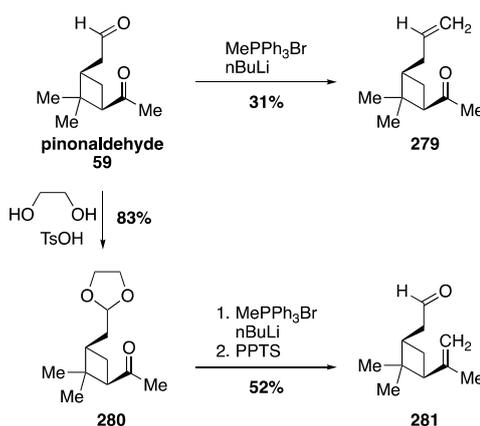
Zhao *et al.* 2021

Figure 45. Synthesis of unsaturated species as ozonolysis probes.

7. Conclusions

The complex products produced by the atmospheric oxidation of volatile terpenes has provided significant stimulation for the development of many creative synthetic pathways to enable their access. Access to these products has enabled verification of tentative assignments made based on initial mass spectrometry data, and has provided important material to investigate the atmospherically-relevant properties of these important constituents of the climate system. More recent work has focused on providing robust access to organosulfate and organonitrate species formed in the atmosphere by the interplay of biogenic terpene species with the products of anthropogenic pollution, while advances in the preparation of isotopically-labelled compounds has enabled a greater understanding of the complex mechanistic pathways involved in the formation of secondary organic aerosol material. Much of the advances made in this area are due to a rich interplay between synthetic organic chemistry, physical chemistry, atmospheric science, and environmental engineering. Given the importance of understanding our climate, continued interdisciplinary efforts supported by synthetic chemistry will likely remain of high value.

8. Conflicts of interest

There are no conflicts to declare.

9. Acknowledgements

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