

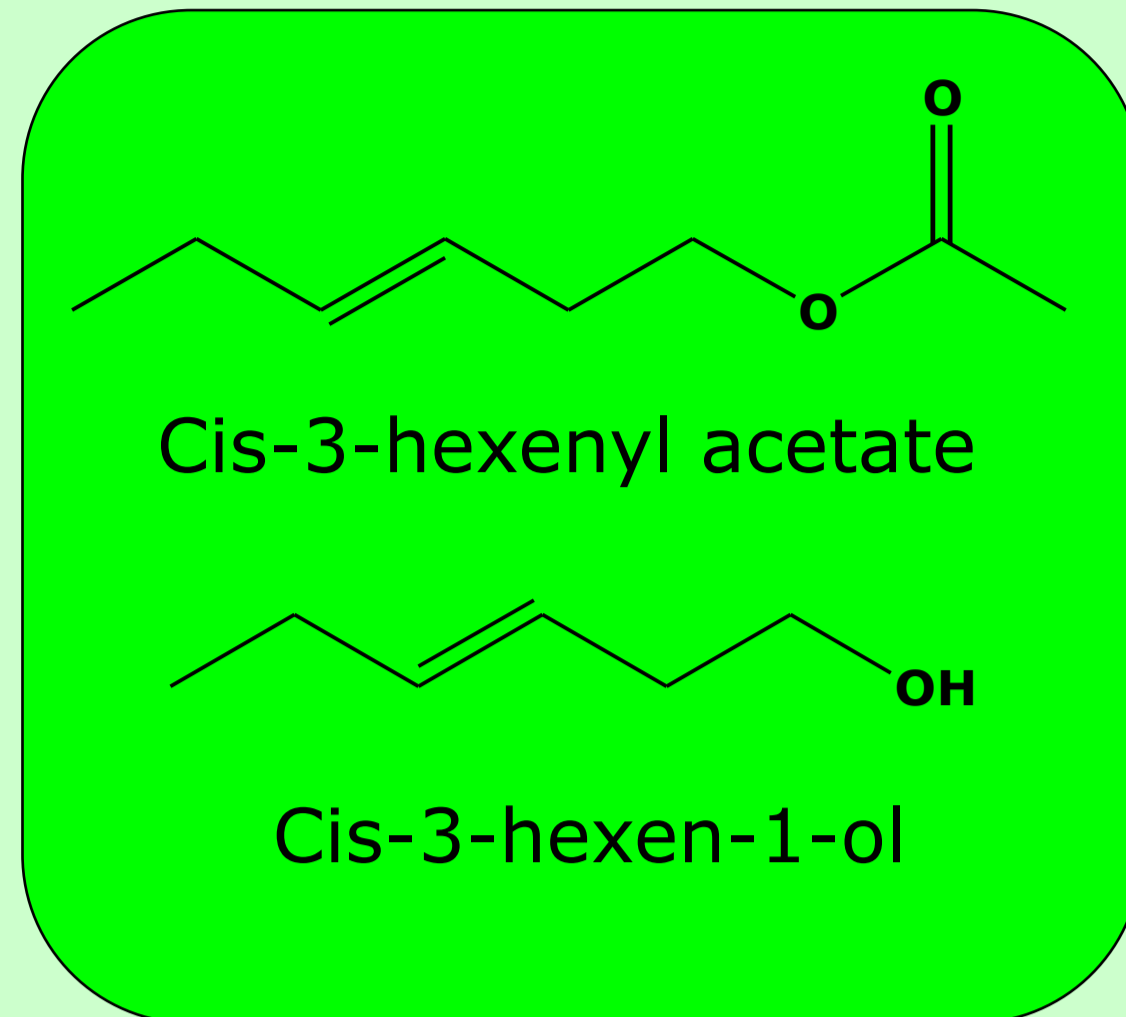
Simulation Chamber Studies of the Reaction of Ozone with C6 Biogenic Oxygenated VOCs

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Introduction

In recent years an increasing number of oxygenated BVOCs have been detected in field measurements and plant emission studies. In particular a range of C6 oxygenates have been identified including compounds such as cis-3-hexenyl acetate and cis-3-hexen-1-ol. Because of their large emission sources, biogenic VOCs play an important role in the chemistry of the troposphere.

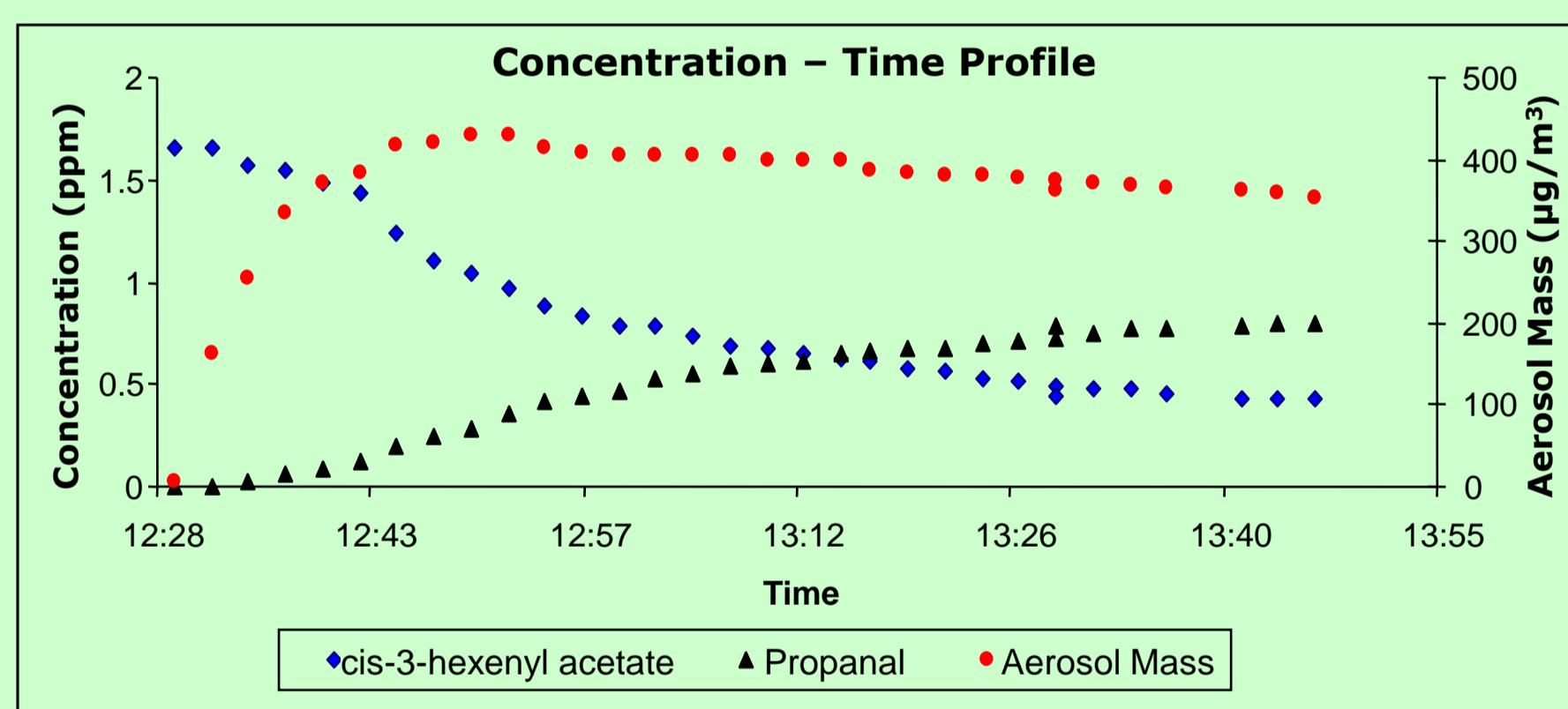


The atmospheric fate of BVOCs is dominated by gas-phase reactions with three species in the troposphere: hydroxyl radical (OH), nitrate radical (NO₃) and ozone (O₃). The aim of this work is to investigate the reaction of ozone with the C6 family of BVOCs under atmospheric conditions and also investigate secondary organic aerosol formation (SOA).

Results

Cis-3-hexenyl acetate & Ozone Reaction

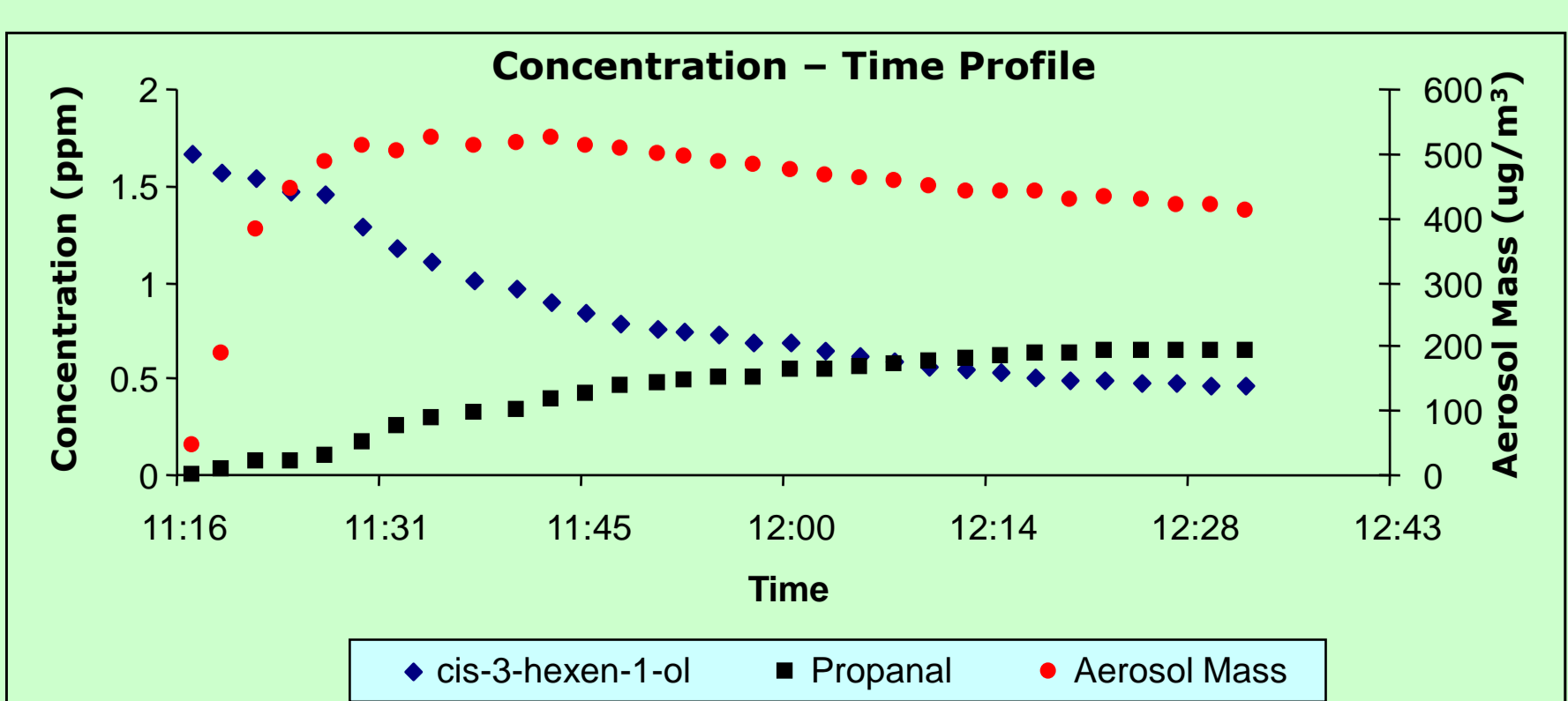
Retention Time	Product	MW of PFBHA Derivative	M/Z
11.4, 11.6	Propanal	253	253 (M) 181 223 (M-30)
17.1	3-oxo-propyl acetate	311	311 (M) 281 (M-30) 130 (-181)
21.5	Methyl Glyoxal	267	267 (M) 181 86 (M-181)



Propanal Yield: 65%

Cis-3-hexen-1-ol & Ozone Reaction

Retention Time	Product	MW of PFBHA Derivative	M/Z
11.4, 11.6	Propanal	253	253 (M) 181 223 (M-30)
15.1	3-Hydroxy Propanal	269	252 (M-17) 239 (M-30) 181
21.5	Methyl Glyoxal	267	267 (M) 181 86 (M-181)



Propanal Yield: 55%

Experimental

Experiments on the O₃ initiated oxidation of cis-3-hexenyl acetate and cis-3-hexen-1-ol were performed in a 3910 L indoor simulation chamber in our laboratory in Cork.



Fig 1. Atmospheric Simulation Chamber.

The chamber is equipped with gas chromatography, GC-MS, and in situ FTIR spectroscopy for chemical analysis along with a scanning mobility particle sizer (TSI 3034) for aerosol measurements. In this work, a derivatisation method coupled with GC-MS was used to identify the products of the ozonolysis reactions. The derivatisation agent is O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) and the process involves the reaction of a carbonyl compound with PFBHA to form an oxime. An Annular Denuder Sampling device was used to collect samples from the chamber for GC-MS analysis.

Annular Denuder Sampling

- 5 channel annular denuder tube
- XAD-4 applied to the denuder walls
- Gases trapped on denuder
- Particles collected on filter

Sorbent coated tube Filter pack

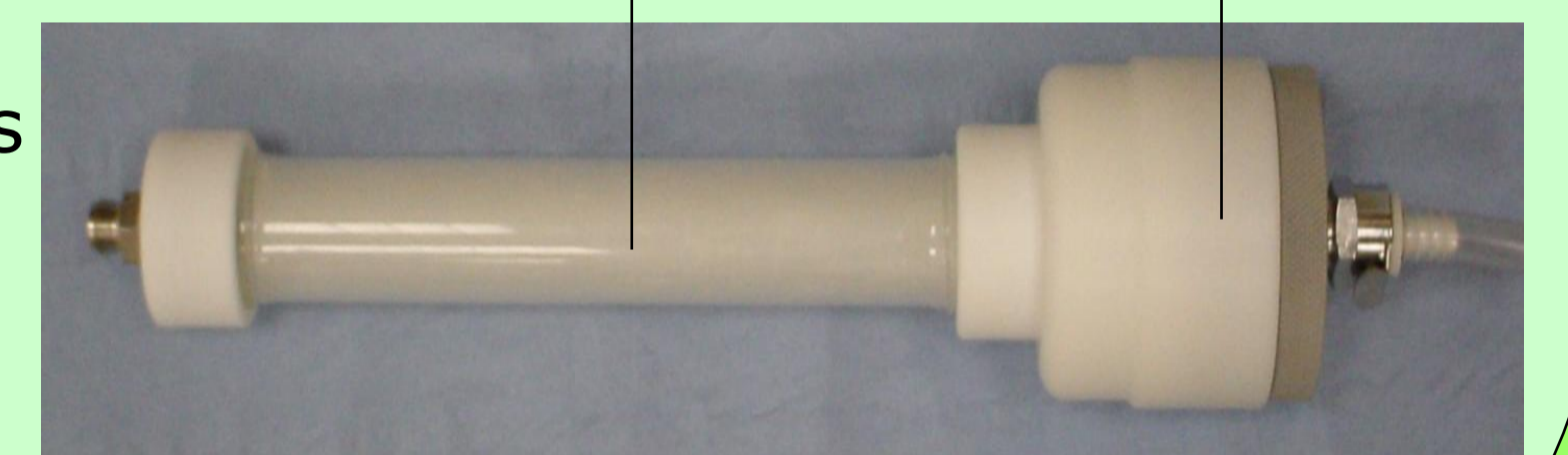
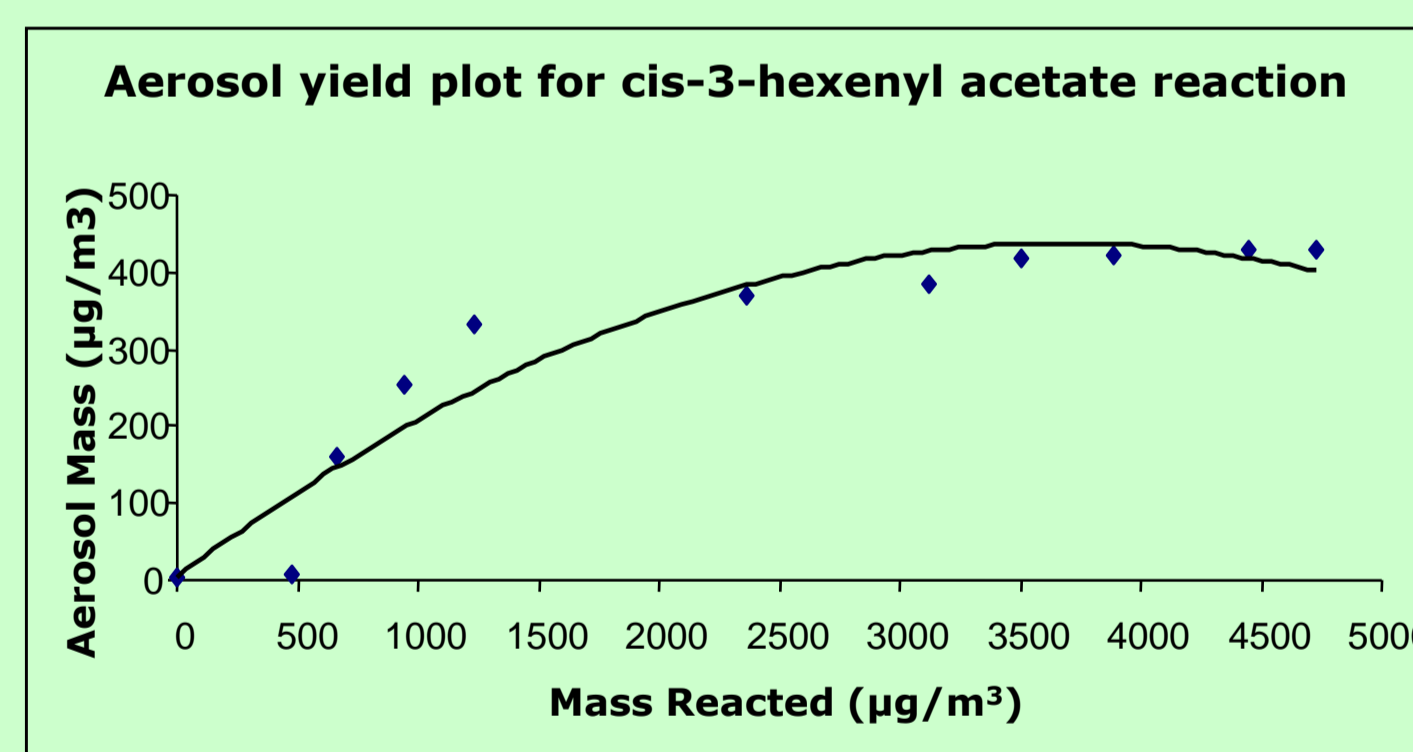
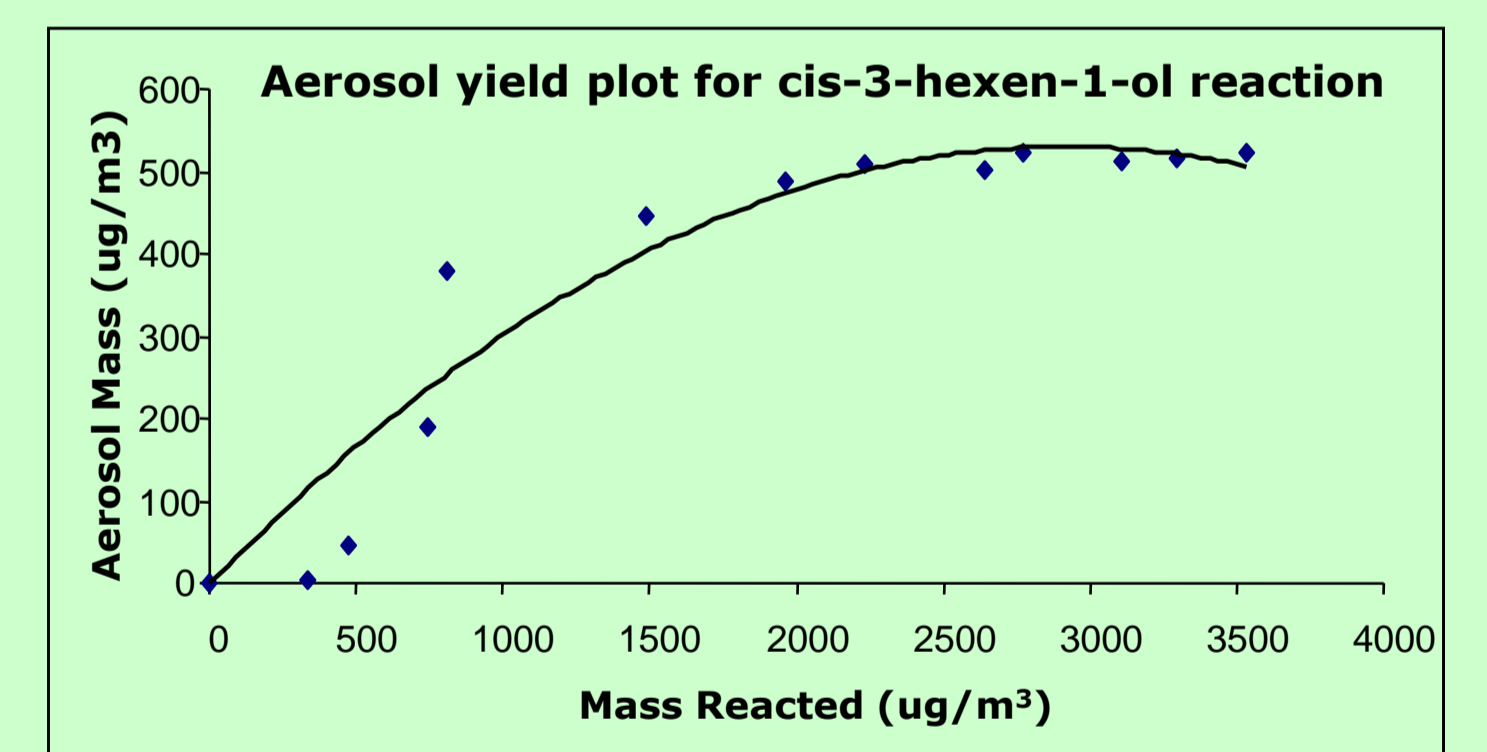


Fig 2. Annular Denuder Sampling Device

SOA Formation



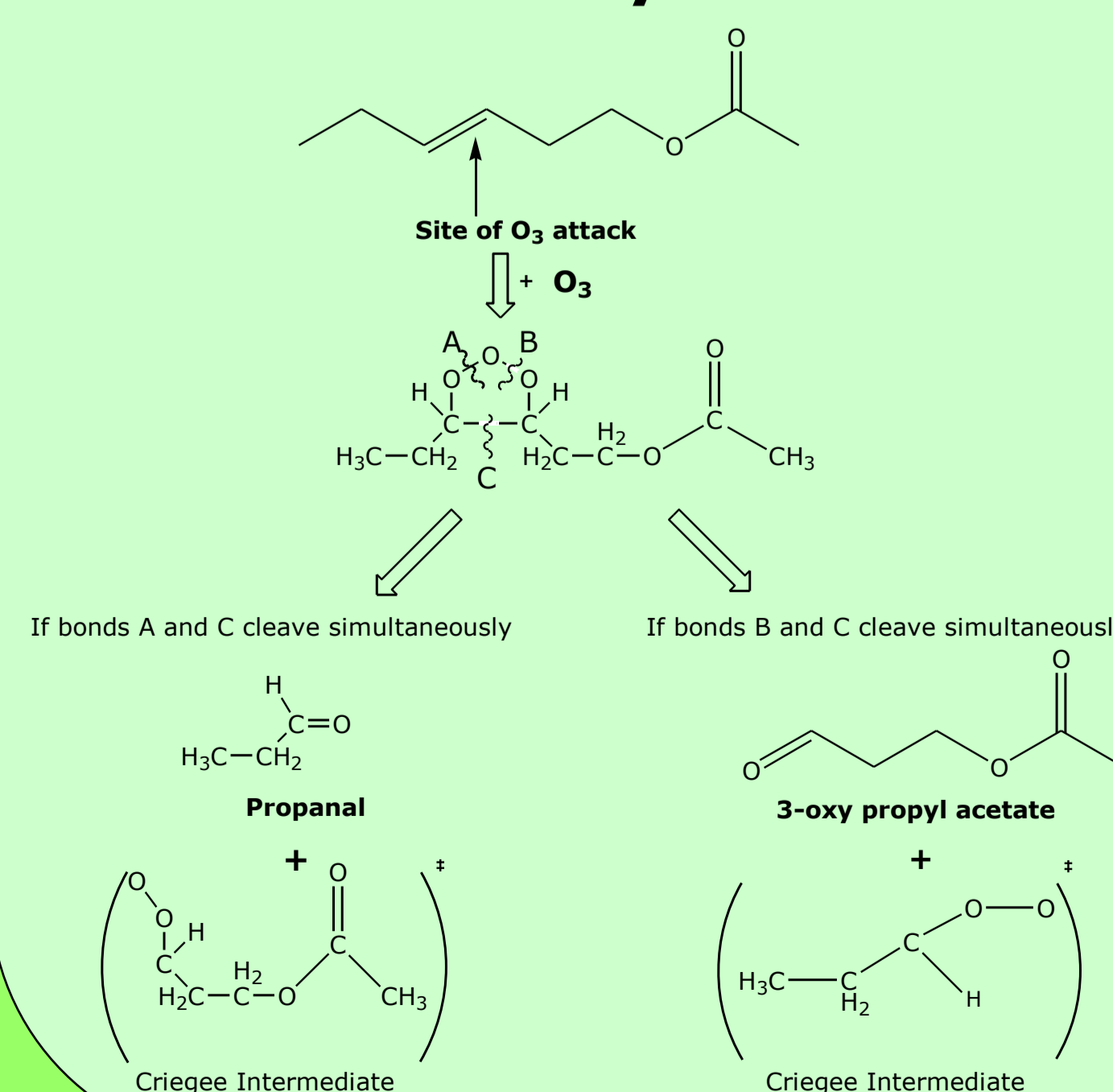
Yield: 15%



Yield: 24%

Reaction Mechanisms

Cis-3-hexenyl acetate



Cis-3-hexen-1-ol

