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Tetrahedron

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Tetrahedron report XXX

## Alkene ozonolysis

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## ARTICLE INFO

## Article history:

Received 12 December 2016

Received in revised form

8 March 2017

Accepted 8 March 2017

Available online xxx

## ABSTRACT

The synthetic application of alkene ozonolysis is reviewed. Emphasis is placed on the scope of potential transformations, traditional and emerging reaction protocols and technologies, comparisons with other oxidations, and safety.

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## 1. Introduction and overview

The reaction of ozone with alkenes, first reported in 1840,<sup>1–5</sup> remains a popular synthetic method,<sup>6</sup> combining operational simplicity with the ability to access a range of products through choice of substrate and conditions. *Scheme 1* summarizes the most common synthetic transformations.

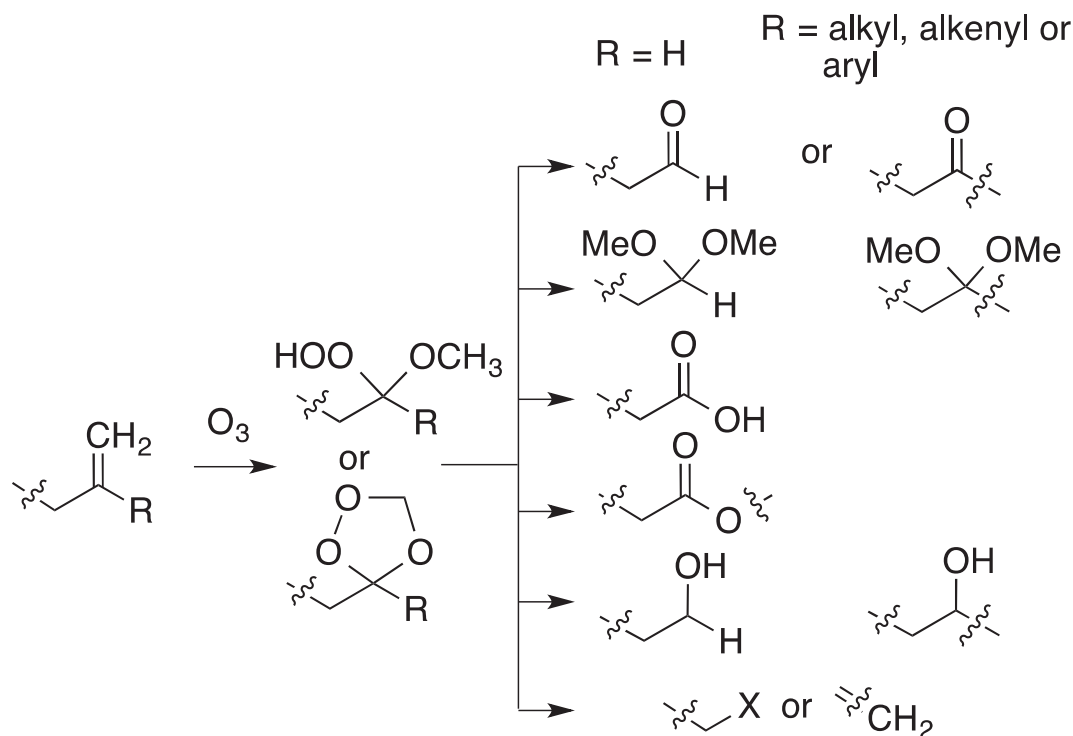
### 1.1. Gateway literature

Bailey's 1978 monograph remains a definitive introduction<sup>7</sup>; other general overviews have since been published.<sup>8–14</sup> A number of reviews or monographs are available on more focused topics, including: the history of ozonolysis<sup>2,15–18</sup>; properties of ozone,<sup>12,19,20</sup> reaction work-ups,<sup>21</sup> application to particular classes of substrates or targets<sup>22–29</sup>; mechanism<sup>30–34</sup>; carbonyl oxides<sup>34</sup>; ozonides<sup>35–37</sup>; reactions at scale<sup>13,28,29,38</sup>; "green" oxidations<sup>39</sup>; the reactivity of silica-absorbed ozone<sup>17,40,41</sup>; and, safety.<sup>42</sup> Leading references are provided to the enormous literature over gas phase ozonolysis.<sup>43,44</sup> A specialized journal, *Ozone: Science & Engineering*,

focuses upon issues related to water treatment and pollutant degradation but also includes reports related to ozone generation, solubility/dispersion, and quantitation.<sup>45</sup> Web sites from industry offer useful information on ozone or ozonolysis.<sup>46</sup> A procedure for an undergraduate laboratory experiment has been described,<sup>47</sup> as has a design of a simple ozone generator.<sup>48</sup> Spectral data for ozonolysis products, including X-ray structures, have been overviewed.<sup>49–51</sup>

### 1.2. Mechanism

The widely accepted Criegee mechanism (*Scheme 2*) begins with dipolar cycloaddition of ozone and an alkene to form a 1,2,3-trioxolane or "primary" ozonide (POZ).<sup>30,52–55</sup> The rate of cycloaddition, discussed in more detail in section 2, typically parallels substrate electron density,<sup>7,56–58</sup> but is also influenced by steric hindrance.<sup>7,59</sup> Most POZs undergo cycloreversion at very low temperature (e.g.  $-100\text{ }^{\circ}\text{C}$ ) to liberate a carbonyl group and a short-lived carbonyl *O*-oxide (hereafter COx).<sup>30,34,60–62</sup> Alternative modes of POZ decomposition are discussed in section 4.



**Scheme 1.** Major classes of products available via alkene ozonolysis.

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