| Imperial College London | Department of Chemistry<br>Third Year Advanced Practical Organic Chemistry |
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# Experiment 6

## Ozonolysis of an Alkene

## EXPERIMENT 6:

# *OZONOLYSIS OF AN ALKENE*

### *Aims of the experiment*

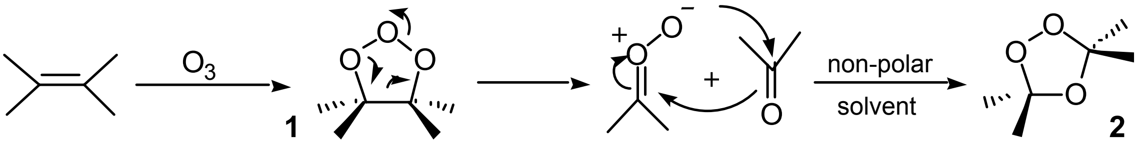
To oxidatively cleave an alkene and trap the resulting carbonyl fragments as their 2,4-dinitrophenylhydrazone derivatives.

### *Techniques used/learned:*

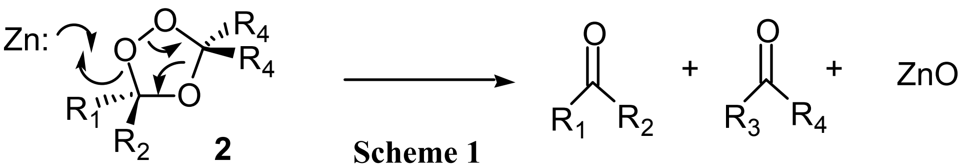
Use of an ozoniser; steam distillation; column chromatography; recrystallisation.

### *Introduction*

Ozone readily attacks ethylenic linkages and from the products, carbonyl compounds can be obtained.[1] The process results in separation of the carbon atoms originally joined by the double bond. The identities and yields of carbonyl products provide information on the positions of the double bonds in the alkene. Hence ozonolysis is frequently used in structure determination as well as for synthetic purposes.
The work of Criegee[2] indicates that the preferred mode of addition to most alkenes is *via* a molozonide **1**. In some cases these can be isolated; reduction at low temperatures can then be made to produce glycols. In general however, the molozonide **1** rapidly decomposes to carbonyl and peroxy (carbonyl oxide) products. These rapidly recombine in non-polar solvents to give an ozonide **2**. Occasionally, a polymer results or the carbonyl oxide may react with polar solvent. Hydrolysis or (preferably) reduction of the the ozonide **2** liberates the two carbonyl compounds.



In the cases where an aldehyde would be formed, the equivalent of peroxide generated by hydrolysis produces carboxylic acid instead of aldehyde. It is therefore preferable to use the reductive work up to reduce the peroxy link. As reducing agents, Zn/AcOH, $Me_2S$, $Ph_3P$, $Me_3P$, and $(NC)_2C{=}C(CN)_2$ have all been used (see Scheme 1): catalytic hydrogenation is hazardous and not recommended. Conversely, treatment of the ozonide with peracids gives ketones and carboxylic acids directly.



**Scheme 1**

Ozonisation is effected by passing a stream of dry ozonised oxygen (1–15% $O_3$) through a solution of the alkene in a suitable solvent (AcOH, $CCl_4$, $CHCl_3$, hexane, EtOAc are all used) at or below room temperature until the ozone is no longer rapidly absorbed.  Over ozonisation will cause general oxidation and decomposition.

# *HAZARD DATA - READ THIS BEFORE GOING ANY FURTHER!*

## OZONE:

**VERY TOXIC BY INHALATION**
**SKIN/EYE IRRITANT**
**EXPLOSIVE WITH REDUCING AGENTS**

A toxic gas which forms explosive ozonides with many alkenes. Avoid inhalation and skin/ eye contact. OEL 0.2 mgm$^{-3}$.

**Toxic effects:** Gas strongly irritates the upper respiratory tract and may cause headache. High concentrations have caused death by lung congestion in animals. Harmful by skin contact.

**Hazardous reactions:** Solid and liquid ozone are highly explosive; forms explosive peroxides with alkenes and other organic molecules. Explodes with many reducing agents; $Br_2$, HBr, $N_2O_4$.

## ACETIC ACID:

**FLAMMABLE**
**CAUSES SEVERE BURNS**

Colourless liquid, with acrid pungent odour; b.p. 118°C, m.p. 17°C. Soluble in water. OEL 25mgm$^{-3}$

**Toxic effects:** Causes severe burns. Causes internal irritation and damage if taken by mouth. Irritiating vapour.

**Hazardous reactions:** Dangerous in contact with chromic acid, sodium peroxide, and nitric acid. Causes vigourous exothermic polymerisation with acetaldehyde.

**Spillage & disposal:** Wash areas with water and then ventilate to dispel residues.

## ZINC (dust):

**FLAMMABLE POWDER**

Grey powder, insoluble in water.

**Toxic effects:** Irritating to eyes. Harmful by ingestion.

**Hazardous reactions:** Reacts with acids to liberate hydrogen.

**Spillage & disposal:** Sweep up spillages and contain for disposal.

## 2,4-DINITROPHENYLHYDRAZINE:

**EXPLOSIVE WHEN DRY**
**TOXIC BY INHALATION, INGESTION AND BY SKIN CONTACT**

Orange-red crystalline powder, slightly soluble in water. Avoid contact with skin, and ingestion.

**Toxic effects:** Toxic by inhalation, ingestion and skin contact. Irritating to eyes and skin. Danger of cumulative effects.

**Hazardous reactions:** Explosive when dry. Can react vigorously with oxidising and reducing reagents.

**Spillage & disposal:** Clear area. Wear goggles, gloves, and laboratory coat. Mix with wet sand and transfer to container for disposal. Wash area with detergent and water.

## OCT-1-ENE:

**HIGHLY FLAMMABLE**

Colourless liquid, characteristic sharp odour; b.p. 122°C. Insoluble in water.

**Toxic effects:** Harmful if ingested in quantity. Irritating to eyes and skin.

**Fire hazard:** Flash point: 21°C. Extinguish fires with $CO_2$.

**Hazardous reactions:** Can react vigorously with oxidising reagents.

**Spillage & disposal:** Clear area. Wear goggles, gloves, and laboratory coat. Mix with sand and transfer to container for disposal. Wash area with detergent and water.

### *Experimental Procedure*

### *General*

Purify a sample of oct-1-ene by distillation before use.

### *The Ozone Generator*

The commercial Triogen generator produces 3.1g/hr of ozone at an oxygen flow rate of 1 l/min [ *i.e.* set the TOP of the spinner on the flow control to 1 l/min]. *Do not deviate from this flow rate.* **The $O_3$/ $O_2$ mixture must be passed through a reversed Drechsel bottle, placed between the generator and the reactor vessel, to prevent suck-back into the generator.** Similarly, after the reactor, the flow should be passed through an empty Drechsel bottle, to catch entrained liquid, and vented high in the fume cupboard. All connections should be securely made with pvc tubing. Have your setup **CHECKED BY A DEMONSTRATOR** before proceeding.

### *Method*

The experiment $O_3$ be carried out in the fume hood dedicated to the ozonolysis experiment. **Keep the hood fully down while passing oxygen and/or ozone-oxygen mixtures through your sample.**

Weigh accurately 0.03125 mole of the pure 1-octene into a large Dreschel bottle containing glacial acetic acid (100 ml). Wash in the last traces with a little acetic acid. Immerse the reactor up to the neck in an ice/water bath and connect into the gas flow system. Turn on the oxygen and adjust the flow rate (to 1 l/min) *before* switching on the generator. When everything is ready, get the set-up checked by a Demonstrator or Technician.

Finally, switch on the generator and pass the $O_3$/$O_2$ mixture for 30 min (0.03125 mole of $O_3$). Switch off the generator and allow the $O_2$ flow to purge the system for a few minutes. Switch off the gas and disconnect the reactor.

Pour the contents of the reactor into a 500 ml round bottom flask containing zinc dust (5 g) and wash the reactor with a little water. Add the washings to the r.b. flask and leave to stand for at least one hour, then set the flask up for steam distillation in the adjacent fume hood (a useful ‘short-cut’ set-up for steam distillation can be found in "Experimental Organic Chemistry", by Harwood and Moody, page p153; 2nd. ed, pp. 157-158). Steam distil as rapidly as possible and continue until the distillate contains insignificant amounts of carbonyl compound as judged by a 2,4-dinitrophenylhydrazine test.

Cool the distillate in ice-water and treat directly with 2,4-dinitrophenylhydrazine in ethanolic mineral acid.[3] After 30 - 60 min, the mixture of derivatives is filtered off, dried and the crude yield recorded.

A small, accurately weighed sample of the crude mixture (ca. 0.5g) is then separated by flash chromatography on silica gel (see experiment 3 for details, including warnings on dangers of silica gel) eluting with dichloromethane - petroleum ether b.p. 40–60°C. Recrystallise each pure derivative from methanol and record the yield, m.p., and n.m.r. and i.r. spectra of each.

### *Write Up*

The write up should conform to *Organic and Biomolecular Chemistry* style (Title, Abstract, Introduction, Results and Discussion, Experimental, References). Your introduction must include discussion of the following points:

**1.** The mechanism of both the ozonolysis you have carried out (bear in mind the solvent is AcOH!) and the formation of the 2,4-DNP derivatives.
**2.** One recent (2003 or later) example from the primary literature of the application of OTHER techniques than ozonolysis for oxidative alkene bond cleavage; extra marks for any examples demonstrating selectivity!

### *References and Notes*

**1.** L.F. Fieser and M. Fieser, 'Reagents for Organic Synthesis', John Wiley, New York, vols, 1–15; P.S. Bailey, *Chem. Rev.*, 1958, 58, 925; P.R. Story, *et al.*, *J. Am. Chem. Soc.*, 1965, 87, 737.
**2.** R. Criegee, *Angew. Chem. Int. Ed. Engl.*, 1975, 14, 745.
**3.** a) A.I. Vogel, 'Practical Organic Chemistry' 4th Edn, Longmans, London, 1978, p. 1112; b) L.M. Harwood and C.J. Moody 'Experimental Organic Chemistry', Blackwell, 1989, p.260; 2nd. ed, 1999, p. 254.