Prilezhaev epoxidation in a continuous flow microreactor

Analysis method setup

The methods below describe the analysis methods as used by *Future*Chemistry and act as a starting point or reference when setting up an analysis method on location.

GC method

GC analysis was performed on a Shimadzu GC 2010 GC-FID equipped with a Quadrex 007 1701 column (length: 10 m, internal diameter: 0.1 mm, film thickness: 0.1 mm).

Table 3: GC program

Parameter	*Value*	*Parameter*	*Value*
Injection volume	1.0 µL	**Split temperature**	250°C
		Pressure	5.0 bar
Temperature program		**Total flow**	400 mL/min
0.0 – 0.8 min	35°C	**Column flow**	1.3 mL/min
0.8 – 4.9 min	40°C/min	**Purge flow**	1.5 mL/min
4.9 – 5.4 min	200°C		

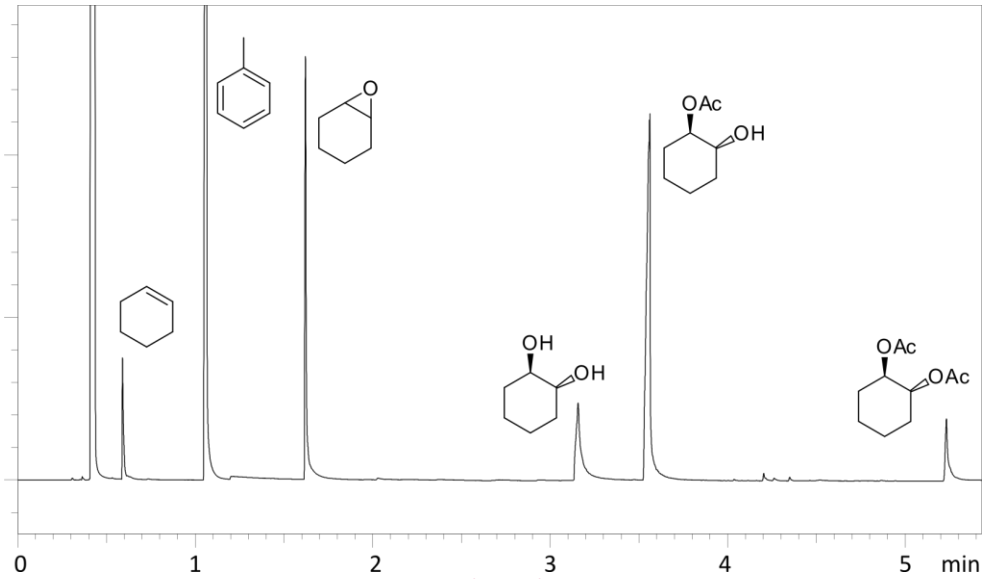

Figure 4: Example GC chromatogram

Table 4: Retention times of internal standard and products

Compound	*Function*	*Retention time [min]*
Cyclohexene (1)	product	0.59
Toluene	internal standard	1.05
Cyclohexene oxide (2)	product	1.63
Cyclohexadiol (3a)	product	3.15
Mono-acetylated diol (3b)	product	3.54
Di-acetylated diol (3c)	product	5.22

Note: The product peaks of the epoxidation samples are visible in the chromatograms. However, quantitative analysis of these compounds is not possible as they are partitioned over the water and DCM layers. Cyclohexene and toluene are, however, fully drawn into the DCM layer and can be analysed quantitatively.

Procedure:

- To set up a valid GC analysis method, first try to analyse a mixture of all components (i.e. a reaction mixture from your Basic Experiment) until all peaks are properly separated. A reference GC program is stated above, which acts as a starting point for your analysis method.
- With the aforementioned mixture, you should observe peaks in roughly the same order as in Figure 4.
- How to solve?
    - If peaks overlap, decrease the temperature gradient (or use isocratic temperature).
    - If analysis takes too long, increase column starting temperature (and vice versa).

Calibrations

To measure percentage conversion of the formed product, a calibration is set up of the substrate against an internal standard as in Table 2, using the concentrations from Table 3.

Table 5: Internal standard/substrate combination

Substrate	***Internal standard***	***Product***
Cyclohexene	Toluene	Epoxide, diol, mono-acetylated diol, di-acetylated diol

Table 6: Calibration samples

Sample	***Toluene***	***Cyclohexene***	***DCM***	***Corresponding conversion***
1	3.00 µL	15.00 µL	400 µL	0%
2	3.00 µL	11.25 µL	400 µL	25%
3	3.00 µL	7.50 µL	400 µL	50%
4	3.00 µL	3.75 µL	400 µL	75%

Procedure:

- Prepare stock solutions of the internal standard (toluene) and the substrate (cyclohexene) in DCM. Use concentrations that can be diluted to the required sample concentrations using the pipettes available in your laboratory. (*The minimum amount you can accurately dispense from a pipette depends on the type and volume.*)
- Prepare four samples as in Table 6.
- Make sure you can analyse your samples with the GC analysis setup. If not, modify the analysis setup until valid chromatograms are obtained.
- From the obtained chromatograms, obtain peak areas.
- Set up a calibration method according to the literature.