DIELS-ALDER REACTION

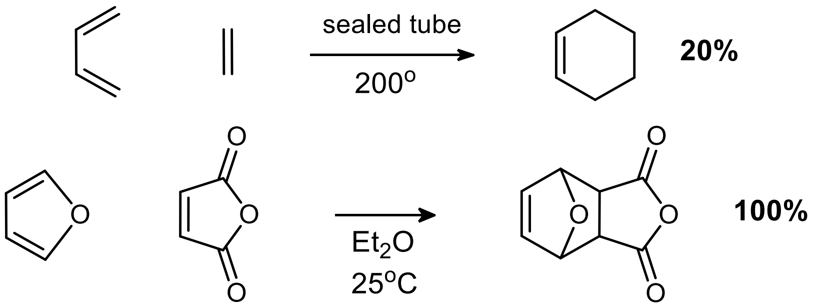
TECHNIQUES REQUIRED : Reflux apparatus, Filtration (Vacuum), Recrystallisation, Melting Point Determination, Yield calculation

OTHER DOCUMENTS Experimental procedure, product spectra

INTRODUCTION

Almost 100 years ago, in 1927, Otto Diels and Kurt Alder treated a constituent of eucalyptus oil with maleic anhydride and isolated a new compound forming “large, lustrous crystals of unusual beauty”. The reaction they discovered now bears their names and they were awarded the 1950 Nobel Prize in chemistry for their work on this reaction. The Diels-Alder reaction[1] is probably the most studied reaction in organic chemistry due to its interest to theoretical, mechanistic and synthetic chemists.

The Diels-Alder reaction is an example of a concerted [4 + 2] cycloaddition of a conjugated diene and a dienophile (alkene or alkyne) that gives access to substituted cyclohexenes in good yield with a very high degree of stereo- and regiochemical control. Both inter- and intramolecular variations are well known. While the simplest example of a Diels-Alder reaction of butadiene and ethene to give cyclohexene is not every efficient (low yielding), reactions with substituted dienes and dienophiles can be far more efficient, as shown by the second example below. In the “normal Diels-Alder reaction”, the nucleophilic diene is made more reactive if substituted with electron donating groups and if locked in the reactive s-cis conformation and the electrophilic dienophile is made more reactive if substituted with electron withdrawing groups. This is illustrated by comparing the efficiency of the two examples shown below:



Examples of Diels-Alder reactions

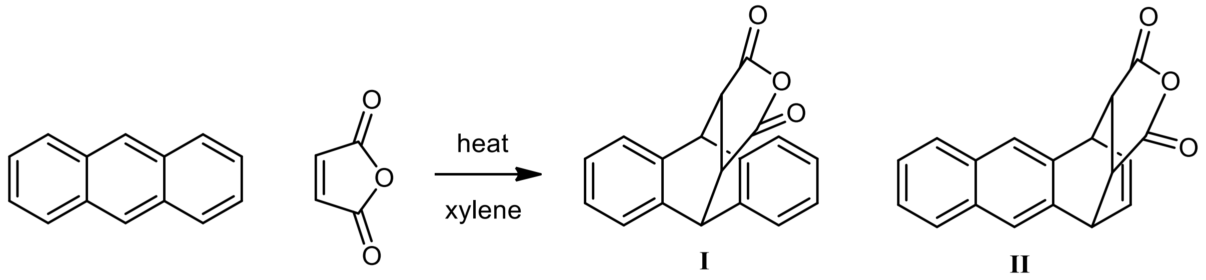
Anthracene[2] was first isolated in 1832 by Dumas and Laurent when they crystallised it from coal tar. Most human exposure to anthracene is from tobacco smoke or from charred foods (*e.g.* barbecued or grilled foods). Anthracene is used in scintillation detectors (for photons, electrons and alpha particles), for fluorescence in forensics and as a wood preservative.

Anthracene is an example of a poly-aromatic hydrocarbon (PAH) based on fused benzene rings. Despite being an aromatic compound, (it contains a cyclic, planar, conjugated pi system that obeys the 4n + 2 “Huckel rule”) that can undergo electrophilic aromatic substitution (EArS), *e.g.* nitration, anthracene also reacts as a conjugated diene undergoing conjugate addition reactions and Diels-Alder reactions since each individual ring is not as effectively stabilised as an isolated benzene ring. This is supported by a comparison of the resonance energies of anthracene (84 kcal/mol) and benzene (36 kacal/mol).

Maleic anhydride[3] was used in the original Diels-Alder reaction and it continues to be a common dienophile for normal Diels-Alder reactions because of the presence electron withdrawing substituents on the alkene unit that make it more reactive. Maleic anhydride is an example of an acid anhydride which are a member of the larger class of compounds of carboxylic acids and derivatives (CAD) that includes acyl chlorides, carboxylic acids, esters and amides. Of these types of functional groups, acid anhydrides are the second most reactive and like the other members of the family, they react with water to undergo hydrolysis to give the parent carboxylic acid. Due to this potential side reaction, it is important that all your glassware is dry. In 2018, about 3.2 metric tonnes of maleic anhydride was produced, with about 50% being used in synthetic resins such as the production of fiberglass.

Xylenes are typically a mixture of three isomeric dimethylbenzenes with a boiling point of 140 °C. At this reflux temperature, it makes a good reaction temperature for this Diels-Alder reaction. Additionally, the freezing point of xylene is about -25 oC so it remains liquid even when cooled in an ice-bath which helps with the purification of the product.

In this experiment, you will be preforming the Diels-Alder reaction of anthracene and maleic anhydride in refluxing xylene, which in principle gives a mixture of two possible Diels-Alder adducts **I** and **II**.



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1 “Organic Chemistry On-Line Learning Center”, Ch 10, https://www.chem.ucalgary.ca/courses/351/Carey5th/Ch10/ch10-5.html.

2. “Wikipedia : Anthracene”, https://en.wikipedia.org/wiki/Anthracene (March 26 2025)

3. “Wikipediia : Maleic anhydride”, https://en.wikipedia.org/wiki/Maleic_anhydride (March 26 2025)

4. E. Singleton, “A greener method for the Diels-Alder reaction using anthracene and maleic anhydride”, https://archive.mcpherson.edu/wp-content/uploads/2022/05/2022302125-SingletonE.pdf