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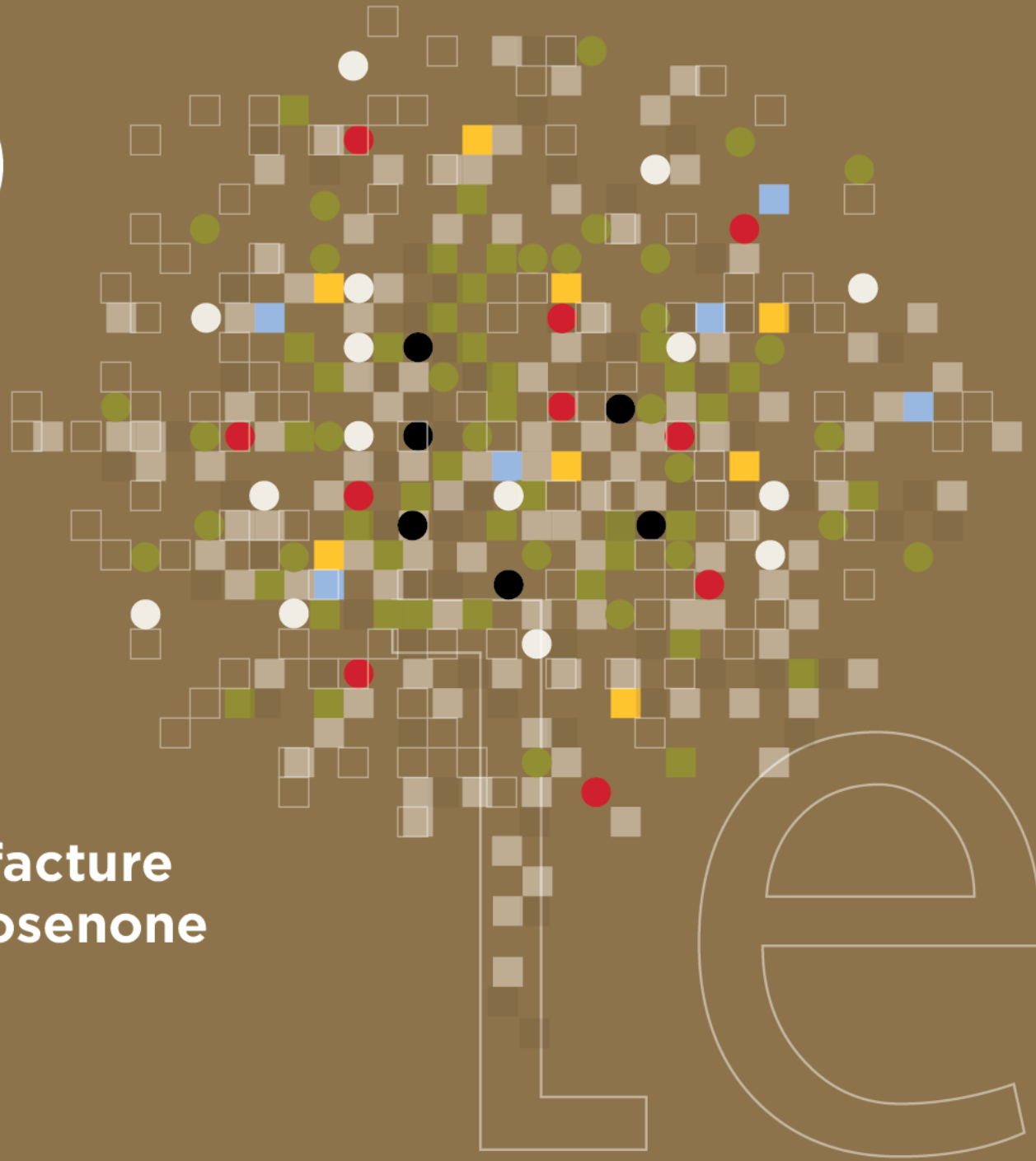
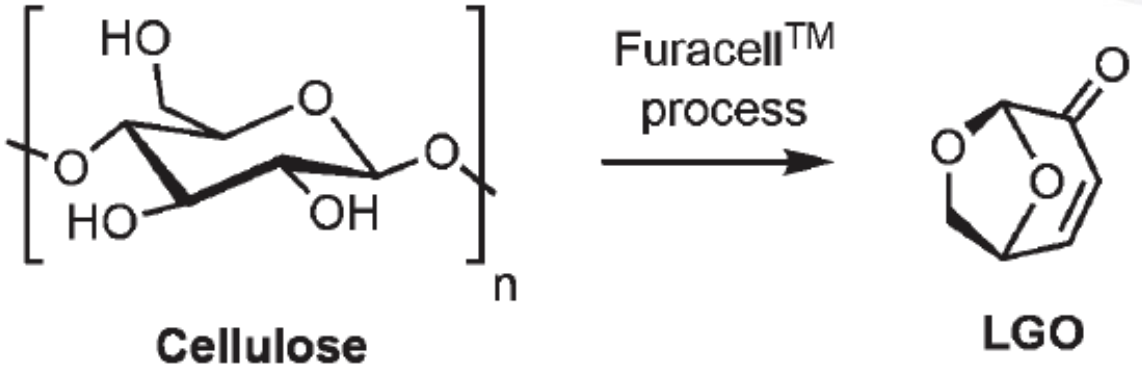
High-performing, Safe and Sustainable Chemicals from Waste Wood

What is Circa Group?



Developers of world's first continuous process to manufacture platform molecule Levoglucosenone from waste cellulose

Our Furacell™ technology



- Proven over **9 years and 4 pilot plants**
- 50T/year **demonstration plant successfully commissioned** and **operated end-to-end**, as of January 2019

Norske Skog

Why Levoglucosenone (LGO)?

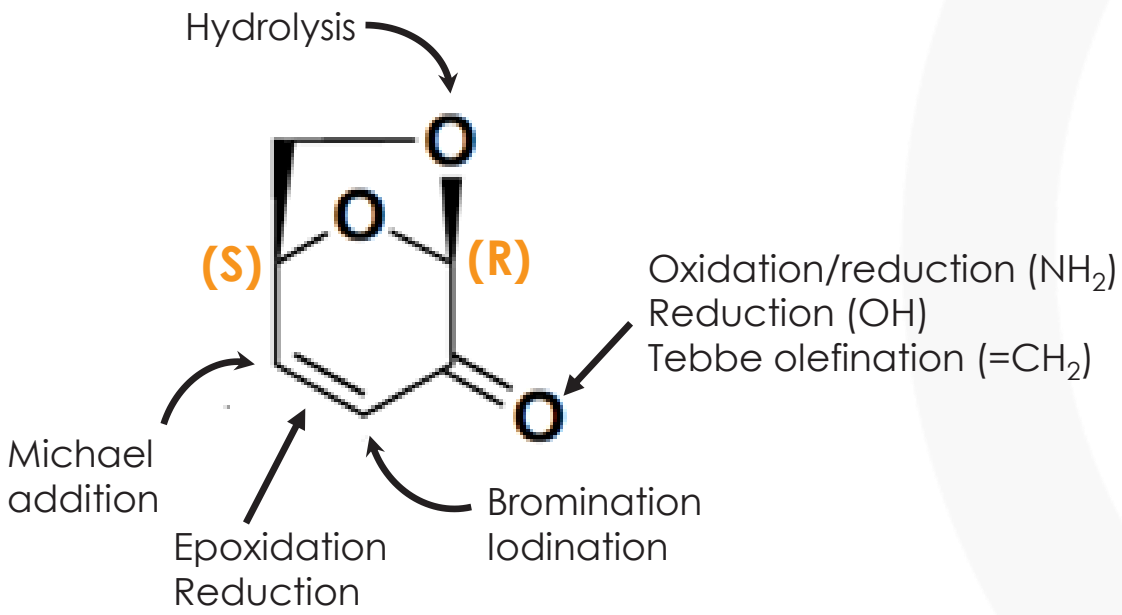


Figure adapted from Witczak, 2017

LGO is a 'bioprivileged molecule'

"A biology derived chemical intermediate that can be efficiently converted to a diversity of chemical products including both novel molecules and drop-in replacements"

(Shanks,2017)

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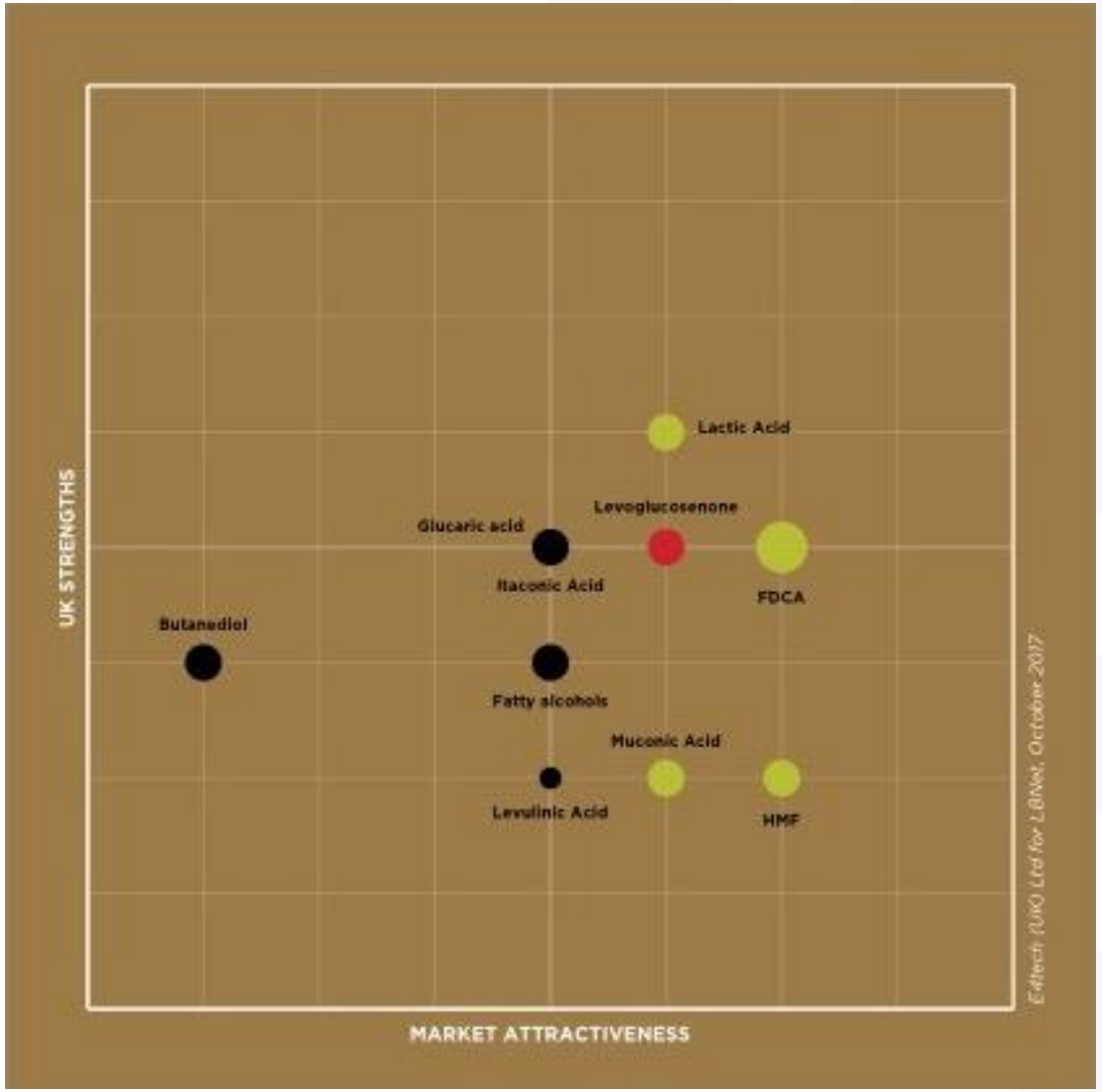
LGO in UK top 3 bio-based chemicals



LBNet
Lignocellulosic Biorefinery Network

E4tech
Strategy | Energy | Sustainability

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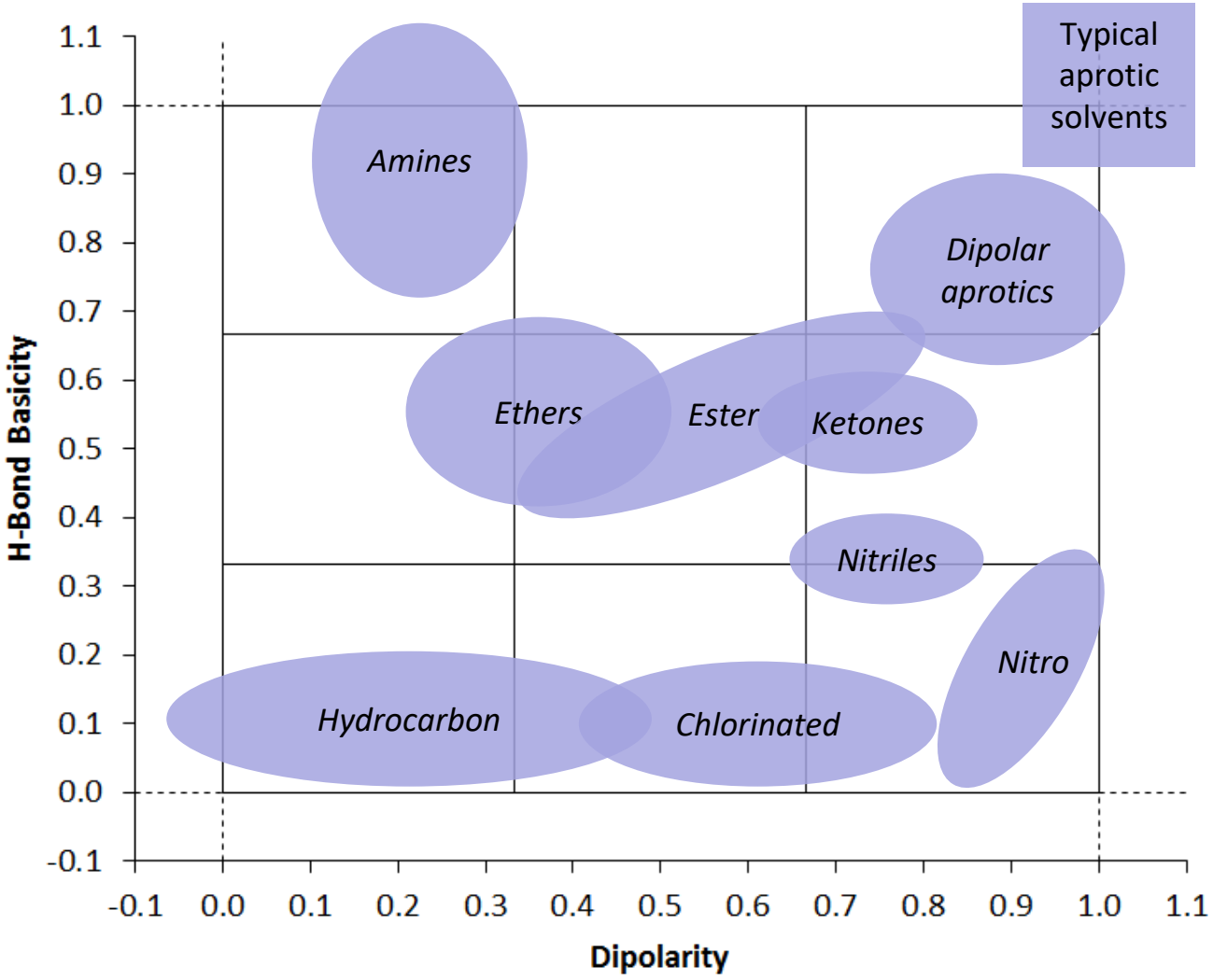
Dehydrolevoglucosenone (Cyrene) – a novel dipolar aprotic solvent

Dehylevoglucosenone (Cyrene)

	Cyrene	NMP	DMF	DMAc
δD (MPa)$^{1/2}$	18.8	18.4	17.4	16.8
δP (MPa)$^{1/2}$	10.6	12.3	13.7	11.5
δH (MPa)$^{1/2}$	6.9	7.2	11.3	10.2
b.p. (°C)	227	202	153	165
η (mPa·s)*	14.5	1.9	0.9	1.0

J. Sherwood *et al.*, *Chem. Commun.*, 2014, 50, 9650



cyrene

NMP added to REACH restricted substances list

Six-year deferral for wire coatings sector

3 May 2018 / Aerospace, automotive & engineering, Alternatives assessment & substitution, Electrical & electronics, Europe, REACH, Restricted substance lists

The European Commission has added 1-methyl-2-pyrrolidone (NMP) to REACH Annex XVII - the restricted substances list.

The substance, which is suspected of being reprotoxic, is already included in Annex XVII under entry 30. This means that any consumer product on the market containing more than 0.3% NMP is prohibited.

The latest restriction proposal, which was made by the Netherlands, was approved by member states at the REACH Committee meeting in October last year.

https://chemicalwatch.com/66647/nmp-added-to-reach-restricted-substances-list

Italy proposes a restriction on industrial and professional uses of N, N-DIMETHYLFORMAMIDE (DMF)[1]

Summary

Italy has submitted an Annex XV dossier under REACH proposing a restriction on the manufacturing, and industrial and professional uses of N, N-Dimethylformamide (DMF, EC No.: 200-679-5).

The basis for this restriction proposal is a concern for human health resulting from the exposure to DMF, due to its reprotoxic properties.

The public consultation on this proposed restriction will start on 19/12/2018 and end on 19/06/2019. However, the rapporteurs of ECHA's Committees for Risk Assessment (RAC) and Socio-economic Analysis (SEAC) would welcome early comments, by 01/03/2019, to assist them in their opinion development.

https://echa.europa.eu/documents/10162/6801c6dd-b022-089e-726e-b4d34941fc63

Dipolar aprotic market

- Represents a > **1,000,000T market**
- In the EU, the solvents dominating this market are:
  - N-methyl-pyrrolidone (NMP)
  - N,N-dimethylformamide (DMF)
  - Dimethylacetamide (DMAc)
- Dipolar aprotic solvents are under **intense regulatory pressure worldwide due to their toxicity**

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Test	Method	Result
Toxicity to reproduction	OECD 422	Negative
Mutagenicity	OECD 471/476/487	Not mutagenic
Acute toxicity (oral)	OECD 423	LD_{50}>2,000mg/kg*
Repeated dose toxicity	OECD 422	NOAEL = 1,000mg/kg/day*
Skin sensitisation	OECD 429	not sensitising
Skin irritation	OECD 404/435	not irritating
Eye irritation	OECD 437/ Ocular Irritection®	Mild eye irritant
Toxicity to fish	OECD 203	96h LC_{50} >100 mg/l*
Toxicity to aquatic invertebrates	OECD 202	48h EC_{50} >100 mg/l*
Toxicity to algae & cyanobacteria	OECD 201	72h EC_{50} >100 mg/l*
Toxicity to microorganisms	OECD 209	3h EC50 >1000 mg/l*
Biodegradability	OECD 301	Readily biodegradable

* maximum concentration tested

Safety

REACH registration to allow sales into EU:

- **Annex VII registration (1-10T)**
  - completed
- **Annex VIII registration (10-100T)**
  - completed

Registration in the US and other jurisdictions to follow

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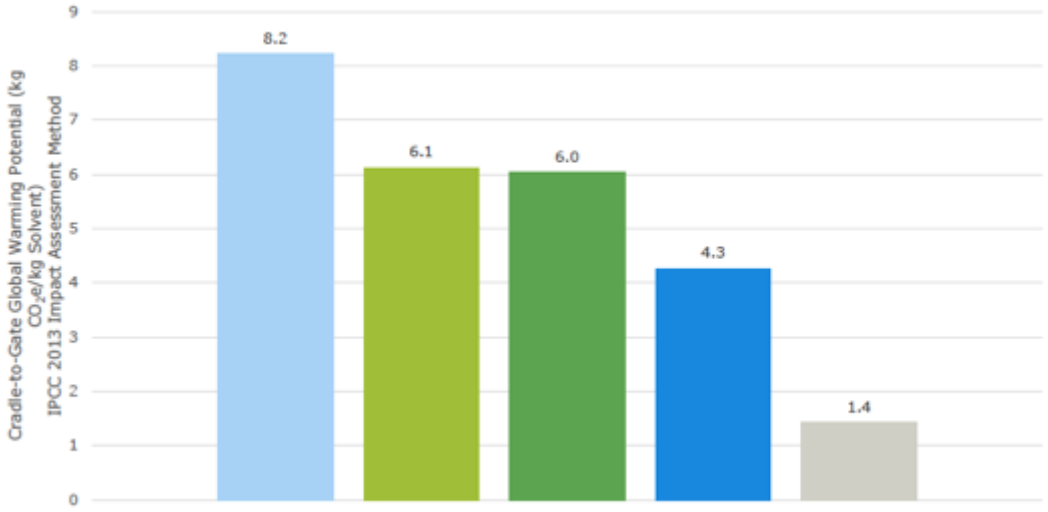

- ANL NMP
- ecoinvent 3.1 NMP, Rest of World
- ecoinvent 3.1 NMP, Europe
- GaBi NMP, Germany
- Cyrene

RAMBOLL ENVIRON

MilliporeSigma

Sustainability

- Feedstock is **non-food competing** and only originates from sustainably managed PEFC and FSC certified forests.
- Cyrene's bio-based content is 98% or 100% depending on source of H_2.
- Independent life-cycle analysis has shown that production of Cyrene using Circa's **Furacell™ process is heading towards being greenhouse gas neutral**.[1]
- Cyrene is readily biodegradable.[2]

[1] Mellentine *et al.*, 2016
[2] OECD 301A test

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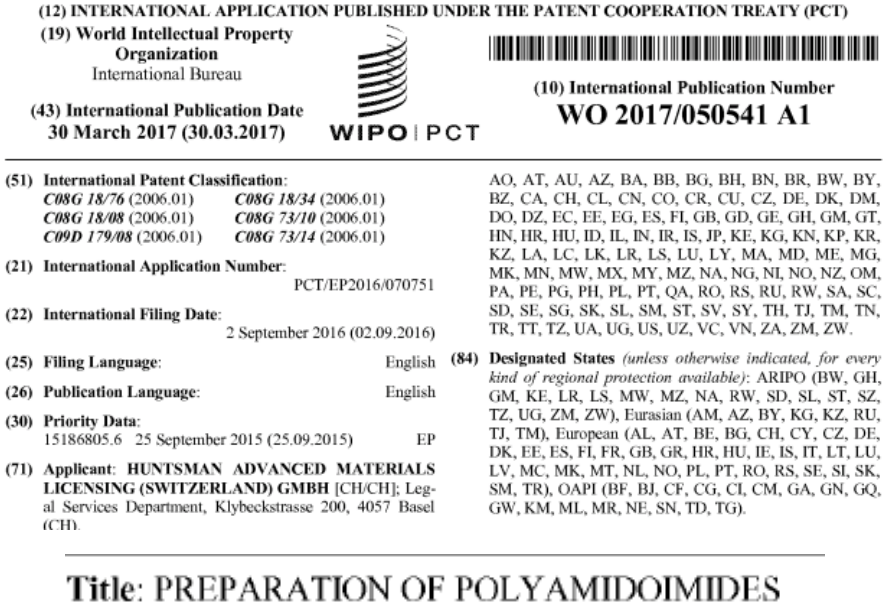

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(71) Applicant: HUNTSMAN ADVANCED MATERIALS LICENSING (SWITZERLAND) GMBH [CH/CH]; Legal Services Department, Klybeckstrasse 200, 4057 Basel (CH).

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Title: PREPARATION OF POLYAMIDOIMIDES

It has surprisingly been found *that the application of dioxabicycloalkane derivatives, and in particular pure Cyrene,* ***instead of conventional polar aprotic solvents like NMP […] not only facilitates rapid curing but also*** *provides* ***coatings having enhanced solvent resistance****.*

Performance:

Polyamide-imides (PAIs) production

- PAIs production – largest user of NMP in European Union[1]
- Wide range of application incl. corrosion resistant coatings
- Cyrene showed to provide a number of benefits vs NMP
- Additional advantage – doesn't produced NOx during curing

[1] EU Restriction report for NMP

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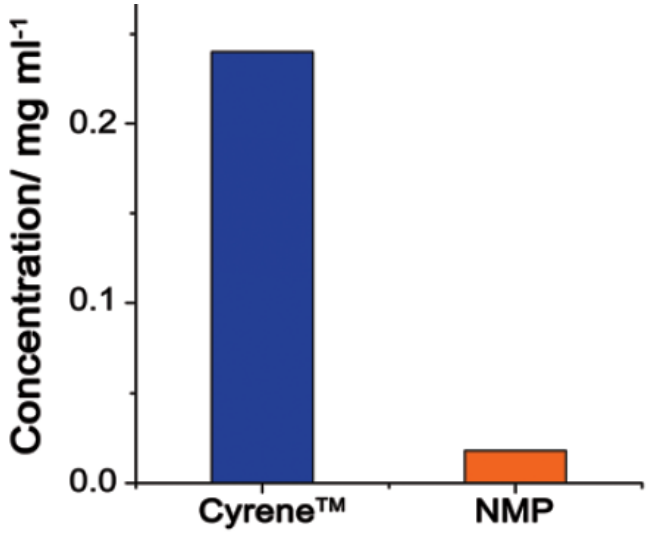

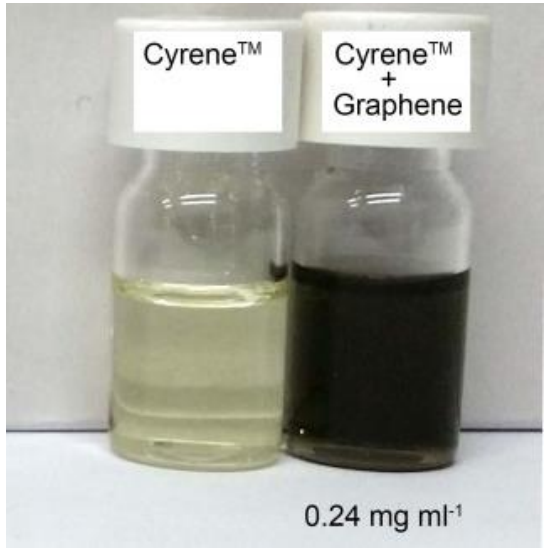

Salavagione *et al.*, *Green Chem.*, 2017, 19, 2550
Pan *et al.*, *Nature Communications*, 2018, 9, 5197

Applications:

Graphene production & dispersion

- NMP widely used to disperse graphene for downstream use
- Wide range of application incl. composites, coatings, batteries, 3D printed materials & functional fluids.
- Cyrene has been shown to have "near ideal physical properties" for the exfoliation of graphite and, crucially, the production of stable, high concentration graphene dispersions and inks

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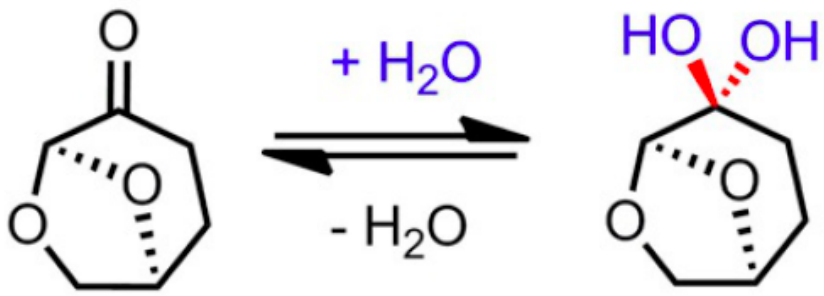
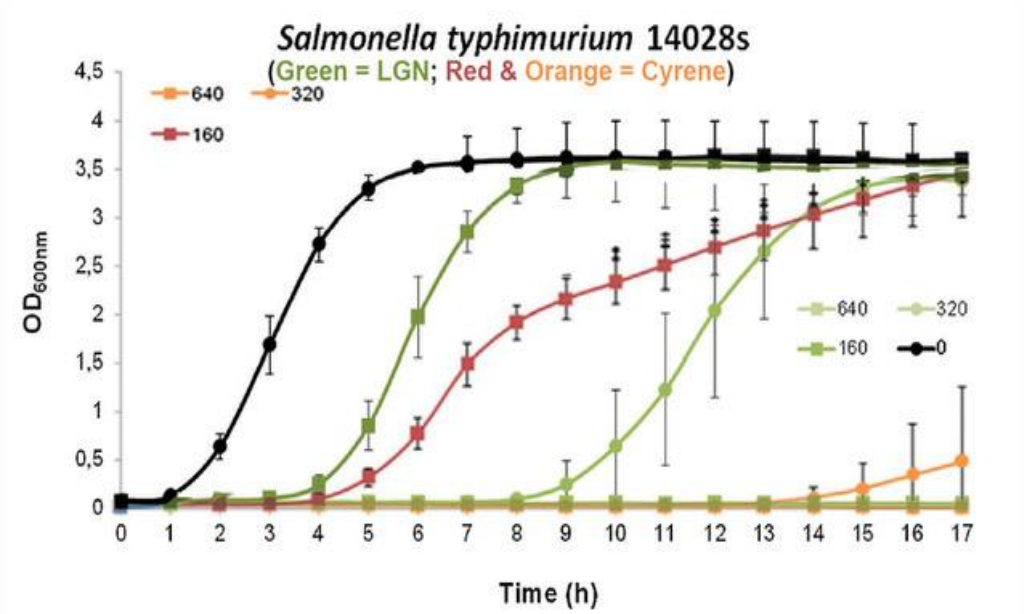
cyrene



Equilibrium between Cyrene and its hydrate in water



De bruyn *et al.*, *ACS Sustainable Chem. Eng.*, 2019, 7, 7878
Giri *et al.*, Industrial Crops & Products, 2017, 105, 113

Applications:
Formulations?

- Adding Cyrene to water been shown to significantly increase the solubility of hydrophobic compounds in water
- This solubility enhancement is due to Cyrene's hydrate, which behaves a hydrotrope
- Cyrene has been shown to be effective against *Salmonella typhimurium* at concentrations of 0.032 and 0.064 weight percent

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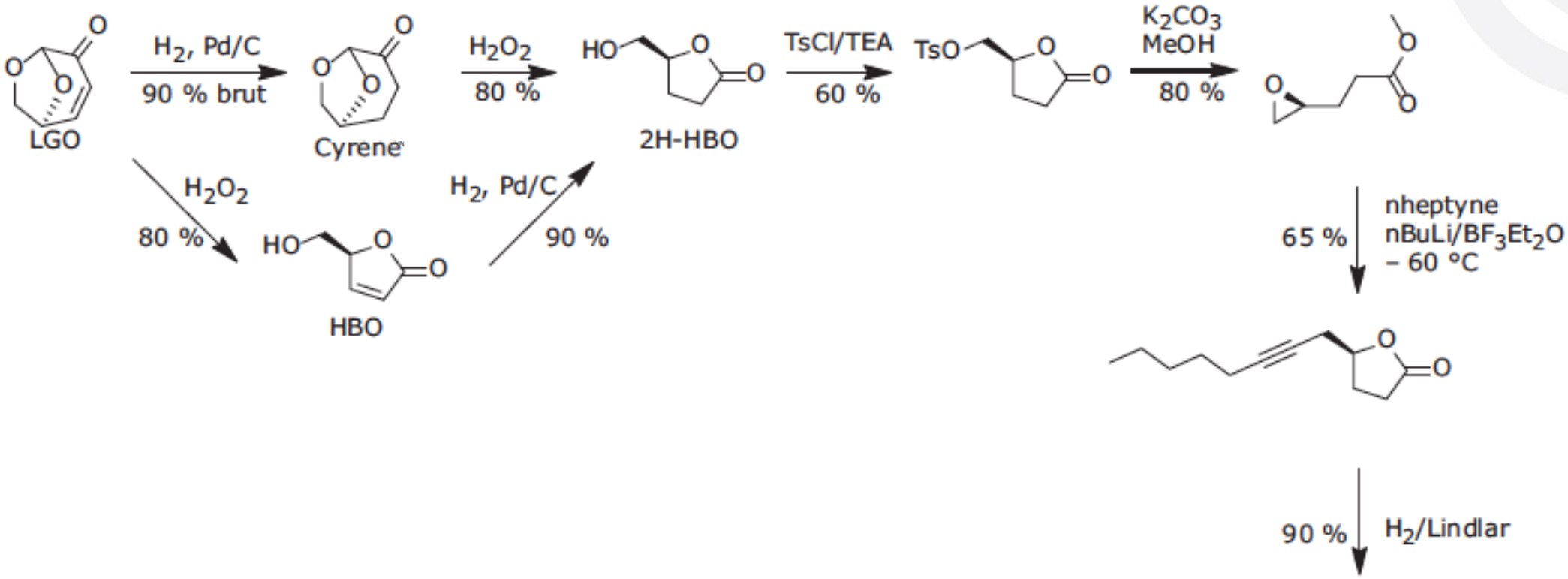
Higher value LGO derivatives

Flavours and fragrances

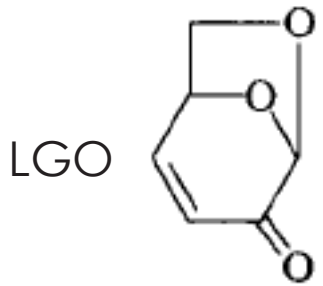


WO Pat. 2016162646, 2016
Bonneau *et al.*, *Green Chem.*, 2018, 20, 2455
Takashi *et al.*, *Heterocycles*, 1990, 31, 1585

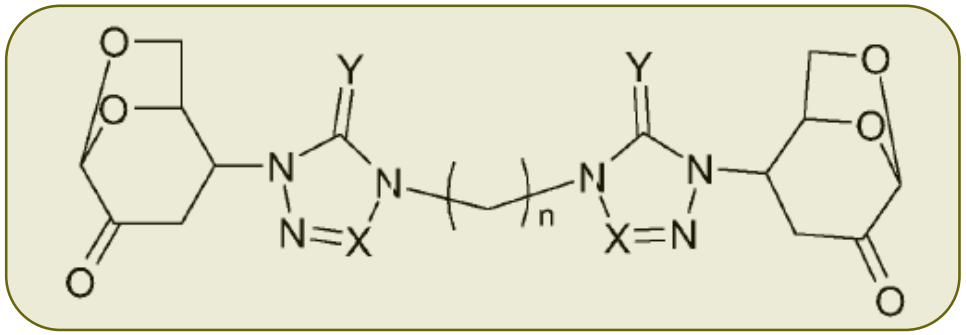
Flavour with a powerful dairy note

CAS 63357-98-2
FEMA 3780

Pharma and agrochemical actives

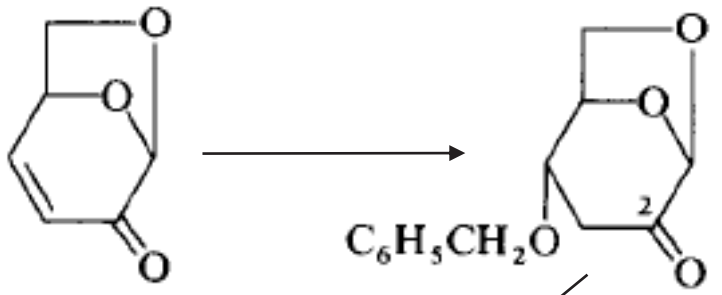


multi steps

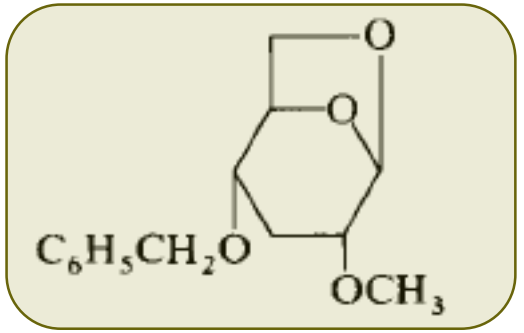


A group of LGO derivatives showing pharmaceutical activity

WO Pat. 139497, 2007



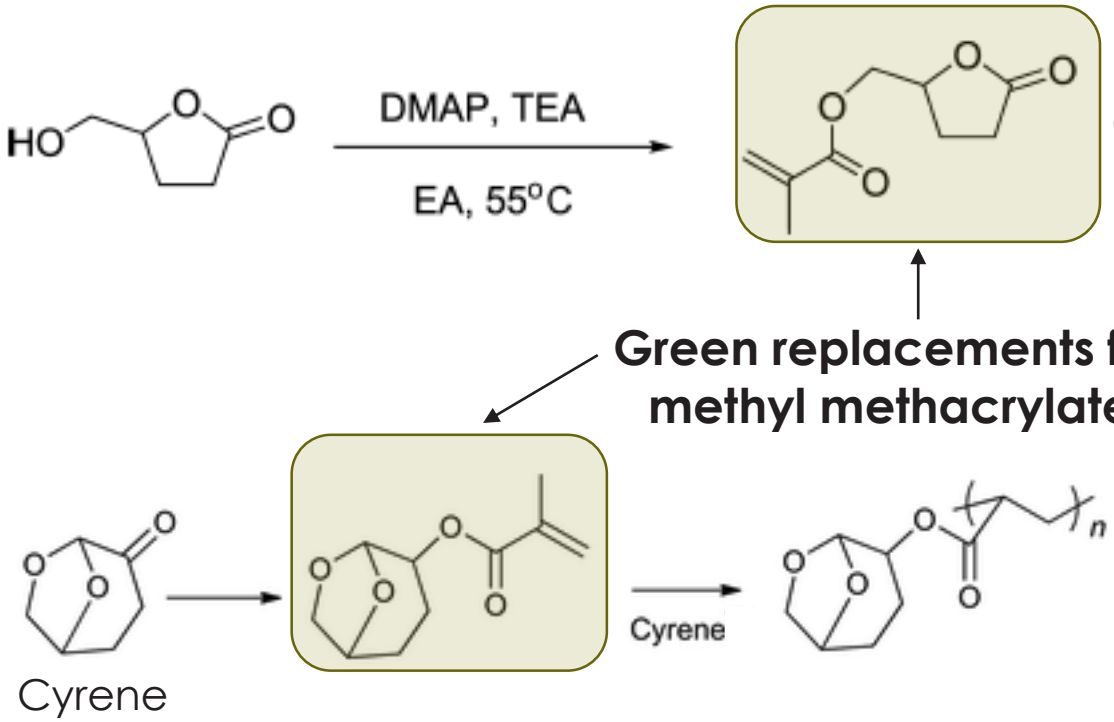
2 steps

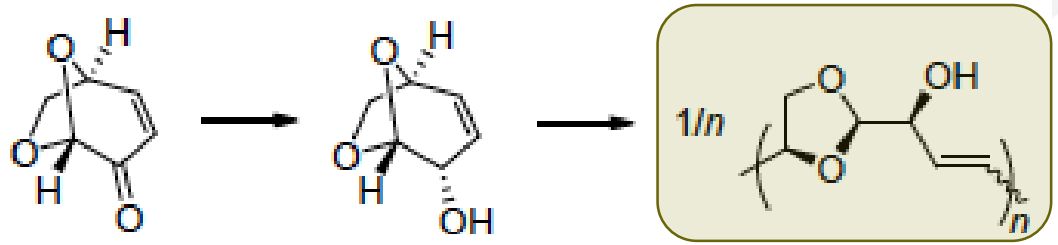


herbicide of considerable potency

Henzell *et al.*, *Pesticide Sci.*, 30 (1990) 59

Polymers





LGO Levoglucosenol Polylevoglucosenol

Transparent and flexible films

Ray *et al.*, ACS Omega 2018, 3, 2040−2048
Diot-Néant *et al.*, ACS Sustainable Chem. Eng. 2018, 6, 17284
Ray *et al.*, *Polym. Chem.*, 2019, Advance Article

Debsharma *et al.*, Angew. Chem. Int. Ed., 2019, 58, 6718

Acknowledgments

Thank you.

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