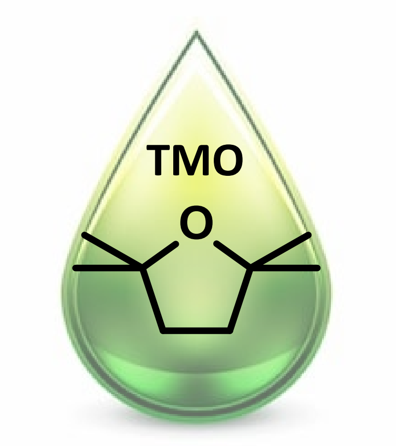
Greener solvents for PSA production

DR. FERGAL BYRNE



This project has received funding from the Bio Based Industries Joint Undertaking under the European Union‘s Horizon2020 research and innovation programme under agreement No 745450.

Resolve project

- 3 year project that started in June 2017 and finished in 2020
- Involves 11 organisations from 5 countries
- Consortium creates a whole value chain
  - From feedstock to solvent producers to end-users
- Aims to find suitable alternatives to Substances of Very High Concern
  - Minimum of one replacement each for toluene and NMP
  - At least comparable performance in relevant applications
  - Improved sustainability, reduced impact on health and the environment.
- Further details at www.resolve-bbi.eu/.

ReSolve
SAFE AND EFFECTIVE BIO-BASED SOLVENTS

UNIVERSITY of York

Project partners

UNIVERSITY of York

WAGENINGEN
UNIVERSITY & RESEARCH

nova Institute
for Ecology and Innovation

Nitto

avantium

circa

BDS
BioDetection Systems

PDC

Norske Skog

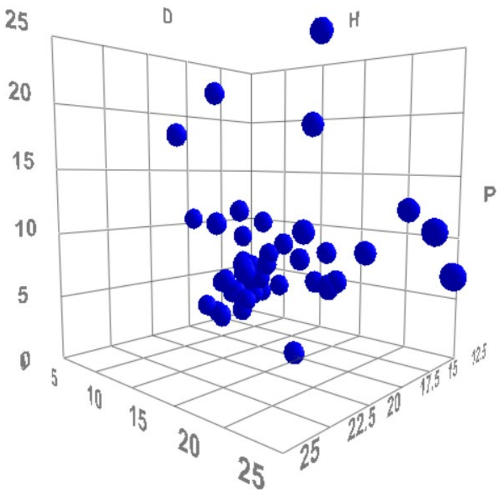
TNO

Bio Base Europe
Pilot Plant

Hazardous Hydrocarbon Solvents

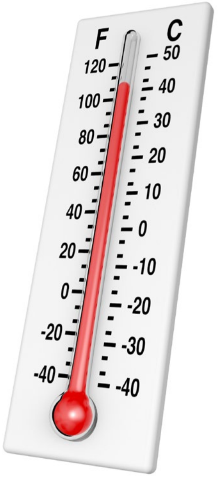
Properties

- High volatility
- Non-polar



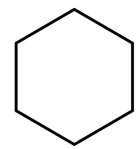
Applications

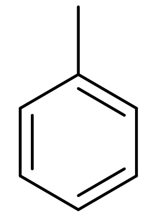
- Reaction media
- Liquid-liquid extractions
- Coating industry



Hazardous Hydrocarbon Solvents

Properties





	Hexane	Cyclohexane	Toluene	
Boiling point / °C	68	81	111	Volatile
δ_D / $MPa^{0.5}$	14.9	16.6	18.0	
δ_P / $MPa^{0.5}$	0.0	0.0	1.4	Low Polarity Low H-bonding
δ_H / $MPa^{0.5}$	0.0	0.0	2.0	

Data taken from PubChem

Hazardous Hydrocarbon Solvents

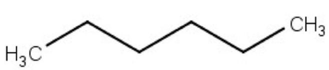
N-hexane

Substance identity

EC / List no.: 203-777-6

CAS no.: 110-54-3

Mol. formula: C6H14



Hazard classification & labelling

Danger! According to the **harmonised classification and labelling** (CLP00) approved by the European Union, this substance may be fatal if swallowed and enters airways, is toxic to aquatic life with long lasting effects, is a highly flammable liquid and vapour, is suspected of damaging fertility, may cause damage to organs through prolonged or repeated exposure, causes skin irritation and may cause drowsiness or dizziness.

Regulatory activities

- Substance included in the Community Rolling Action Plan (CoRAP).

Data taken from ECHA – Information on Chemicals

Hazardous Hydrocarbon Solvents

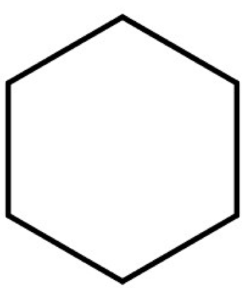
Cyclohexane

Substance identity

EC / List no.: 203-806-2

CAS no.: 110-82-7

Mol. formula: C6H12



Hazard classification & labelling

Danger! According to the **harmonised classification and labelling** (CLP00) approved by the European Union, this substance may be fatal if swallowed and enters airways, is very toxic to aquatic life, is very toxic to aquatic life with long lasting effects, is a highly flammable liquid and vapour, causes skin irritation and may cause drowsiness or dizziness.

Properties of concern

PBT

Regulatory activities

- Some uses of this substance are restricted under Annex XVII of REACH.

Data taken from ECHA – Information on Chemicals

Hazardous Hydrocarbon Solvents

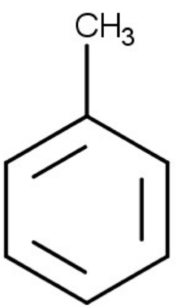
Toluene

Substance identity

EC / List no.: 203-625-9

CAS no.: 108-88-3

Mol. formula: C7H8



Hazard classification & labelling

Danger! According to the **harmonised classification and labelling** (CLP00) approved by the European Union, this substance may be fatal if swallowed and enters airways, is a highly flammable liquid and vapour, is suspected of damaging the unborn child, may cause damage to organs through prolonged or repeated exposure, causes skin irritation and may cause drowsiness or dizziness.

Additionally, the classification provided by companies to ECHA in **REACH registrations** identifies that this substance is suspected of damaging fertility or the unborn child, is harmful to aquatic life with long lasting effects and causes serious eye irritation.

At least one company has indicated that the substance classification is affected by impurities or additives.

Regulatory activities

- Substance included in the Community Rolling Action Plan (CoRAP).
- Some uses of this substance are restricted under Annex XVII of REACH.

Data taken from ECHA – Information on Chemicals

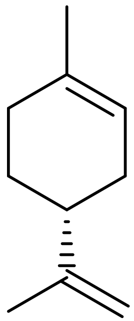
Alternatives

Green solvent requirements

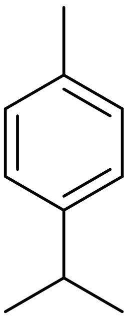
Easy to synthesise	*Few steps from biomass*
Safe	*Non-toxic, non-peroxide forming in storage conditions*
Easy to remove	*But not too easy to remove (bp 70-140 °C)*
Low-polarity	*Not necessarily exact replica of traditional hydrocarbons*
High-performance	*Must not interfere with product formation*
Sustainable	*The use of sustainably-grown biomass waste*
Cost efficient	*Must compete with petrochemicals*

Alternatives

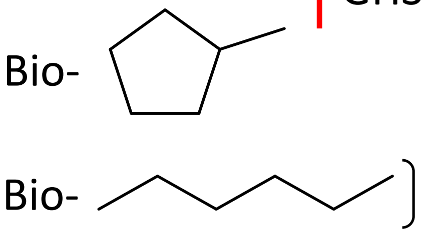
Hydrocarbons



Limonene



p-Cymene



Alkanes

	Limonene	*p*-Cymene	Alkanes
Boiling point / °C	177-178	176-178	72 (68)
δ_D / $MPa^{0.5}$	17.2	17.3	14.4 (14.9)
δ_P / $MPa^{0.5}$	1.8	2.4	0.0
δ_H / $MPa^{0.5}$	4.3	2.4	0.0

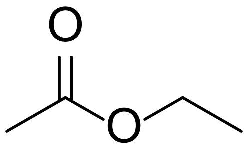
Limonene and *p*-cymene: Difficult to remove

Alkanes: Too volatile

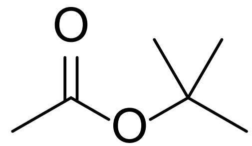
Data taken from PubChem

Alternatives

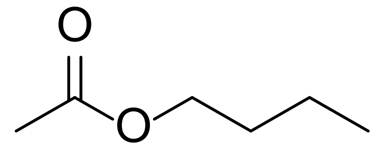
Esters and ketones



Ethyl acetate



t-Butyl acetate



n-Butyl acetate

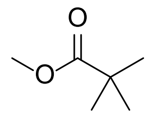
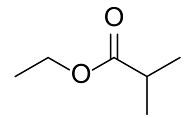
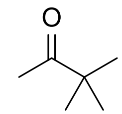
	Ethyl acetate	*t*-Butyl acetate	*n*-Butyl acetate
Boiling point / °C	77	96	126
δ_D / $MPa^{0.5}$	15.8	15.0	15.8
δ_P / $MPa^{0.5}$	5.3	3.7	3.7
δ_H / $MPa^{0.5}$	7.2	6.0	6.3

Increasing Bp

Increasing polarity

Data taken from PubChem

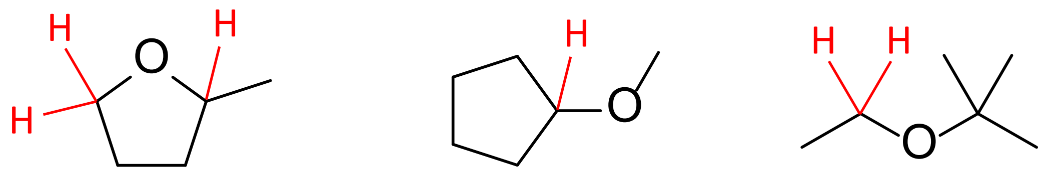
Optimal esters and ketones

Solvent property	Toluene	 Methyl pivalate	 Ethyl isobutyrate	 Pinacolone
Boiling point / °C	111	100-101	108-110	105-106
Melting point / °C	-95	-70	-88	-93
Density / $g \cdot ml^{-1}$	0.867	0.875	0.865	0.803
Autoignition temp. / °C	522	443	451	428
Lower explosion limit / v/v%	1.1	1.3	0.9	1.3
δ_D / $MPa^{0.5}$	18.0	15.0	15.8	15.1
δ_P / $MPa^{0.5}$	1.4	3.8	4.9	5.5
δ_H / $MPa^{0.5}$	2.0	5.0	6.2	5.1
α	0.00	0.00	0.00	0.00
β	0.10	0.45	0.48	0.58
π^*	0.51	0.49	0.51	0.49
Log $P_{(o/w)}$	2.73	1.74	1.54	1.21

F. P. Byrne, B. Forier, G. Bossaert, C. Hoebers, T. J. Farmer and A. J. Hunt, "A methodical selection process for the development of ketones and esters as bio-based replacements for traditional hydrocarbon solvents." *Green Chemistry*, 2018, **20**, 4003–4011.

Alternatives

Ethers



2-MeTHF CPME ETBE

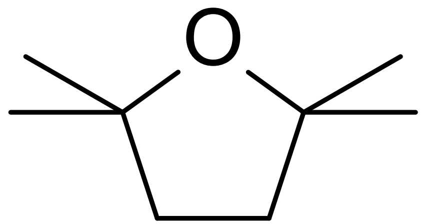
All form explosive peroxides in storage

	2-MeTHF	CPME	ETBE
Boiling point / °C	78-80	106	72
δ_D / $MPa^{0.5}$	16.9	16.7	14.4
δ_P / $MPa^{0.5}$	5.0	4.3	3.5
δ_H / $MPa^{0.5}$	4.3	4.3	2.7

Ideal Bp and HSPs

Data taken from PubChem

2,2,5,5-Tetramethyloxolane (TMO)



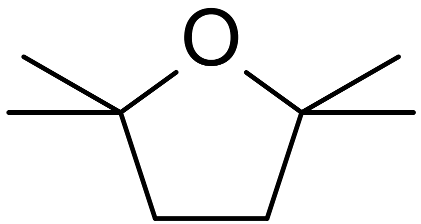
Green solvent requirements

Easy to synthesise	*Few steps from biomass*
Safe	*Non-toxic, non-peroxide forming in storage conditions*
Easy to remove	*But not too easy to remove*
Low-polarity	*Not necessarily exact replica of traditional hydrocarbons*
High-performance	*Must not interfere with product formation*
Sustainable	*The use of biomass waste*
Cost efficient	*Must compete with petrochemicals*

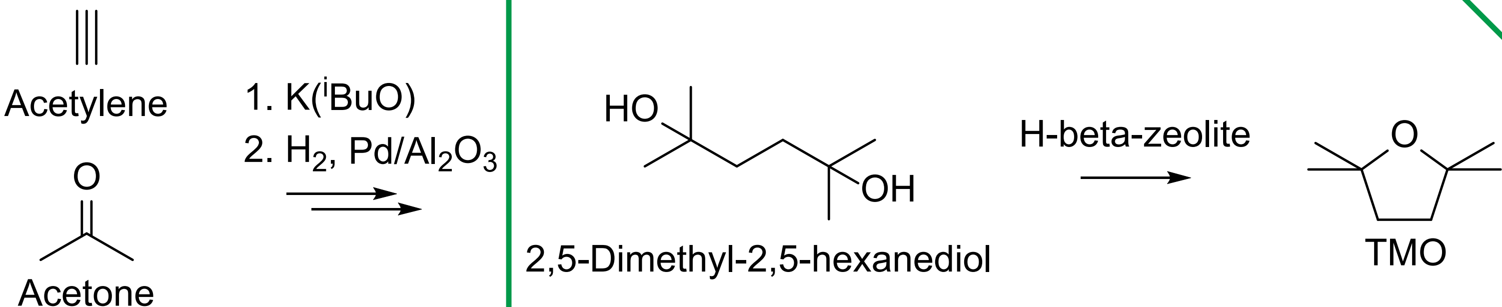
F. Byrne, B. Forier, G. Bossaert, C. Hoebers, T. J. Farmer, J. H. Clark, and A. J. Hunt. “2,2,5,5-Tetramethyltetrahydrofuran (TMTHF): A Non-Polar, Non-Peroxide Forming Ether Replacement for Hazardous Hydrocarbon Solvents.” *Green Chemistry*, 2017, **19**, 3671–78.

2,2,5,5-Tetramethyloxolane (TMO)

Synthesis



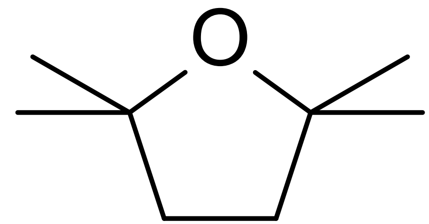
Patented by Nitto
WO2018033635 (A1)



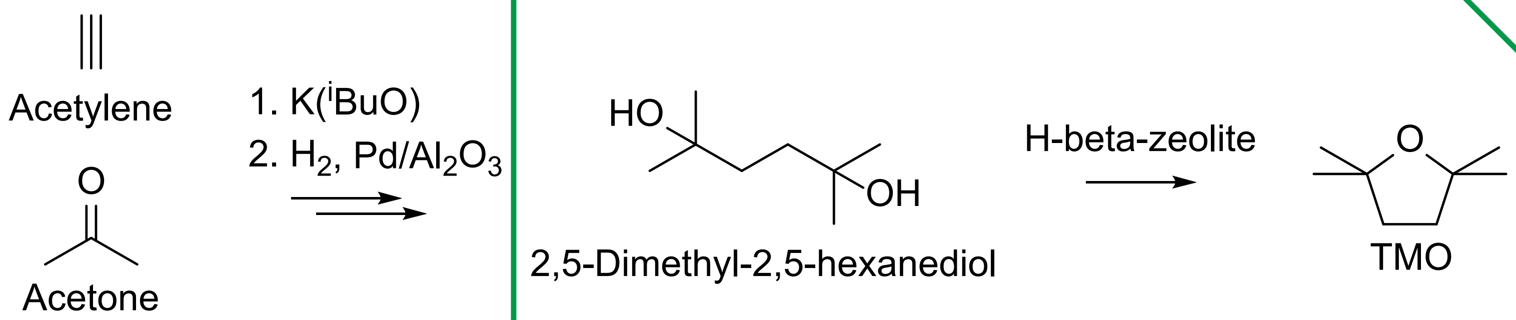
- Conversion = 100%
- Selectivity = >99%
- Process Atom Economy (AE) = 96%
- Reaction Mass Efficiency (RME) = 93%

2,2,5,5-Tetramethyloxolane (TMO)

Synthesis



300 L synthesis carried out at BBEPP in Belgium



- Conversion = 100%
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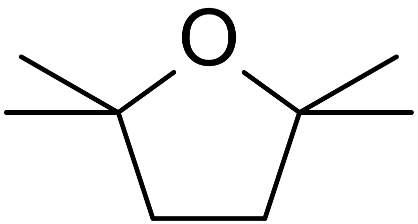
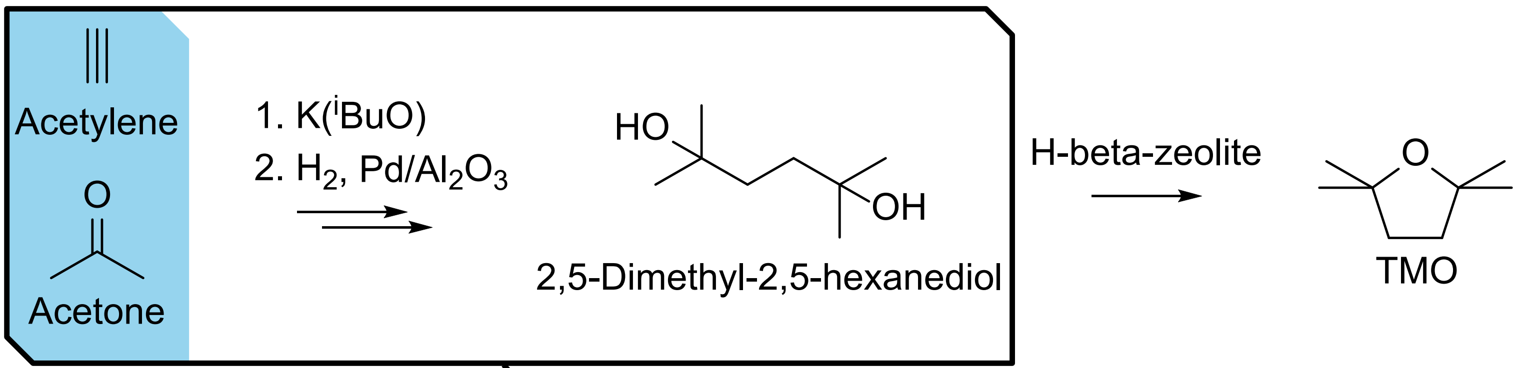
2,2,5,5-Tetramethyloxolane (TMO)

Synthesis



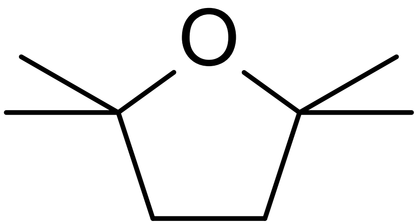


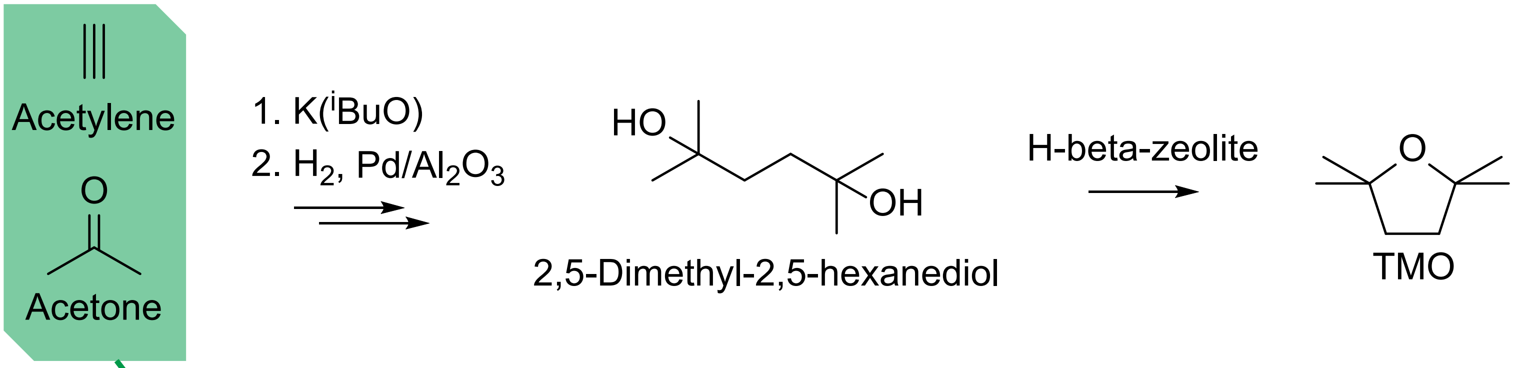
BASF patented process (US6956141 B1)

2,5-Dimethylhexane-2,5-diol used for polymers

2,2,5,5-Tetramethyloxolane (TMO)

Synthesis



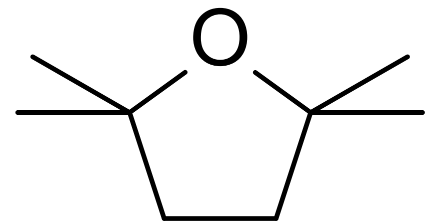


Technically easy to produce from biomass

- Acetylene from partial combustion of methane
- Acetone from ABE fermentation

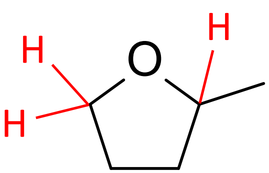
2,2,5,5-Tetramethyloxolane (TMO)

Non-peroxide forming ether

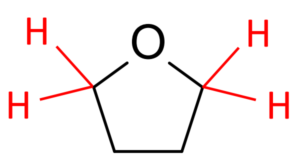


Traditional ethers

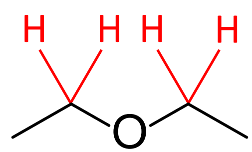
- Abstractable *alpha* hydrogens
- Removed radically is ambient conditions



2-MeTHF



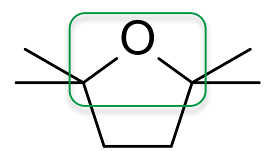
THF



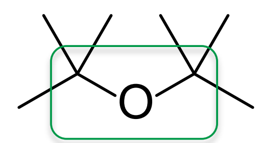
Diethyl ether

Quaternary ethers

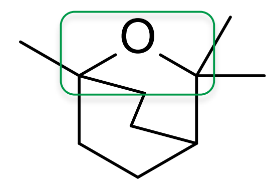
- Unabstractable *alpha* methyl groups
- Very difficult to remove



TMO

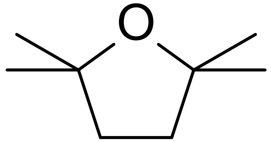


DTBE



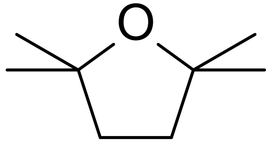
Eucalyptol

F. Byrne, B. Forier, G. Bossaert, C. Hoebers, T. J. Farmer, J. H. Clark, and A. J. Hunt. “2,2,5,5-Tetramethyltetrahydrofuran (TMTHF): A Non-Polar, Non-Peroxide Forming Ether Replacement for Hazardous Hydrocarbon Solvents.” *Green Chemistry* 19, 3671–78. https://doi.org/10.1039/C7GC01392B.



TMO

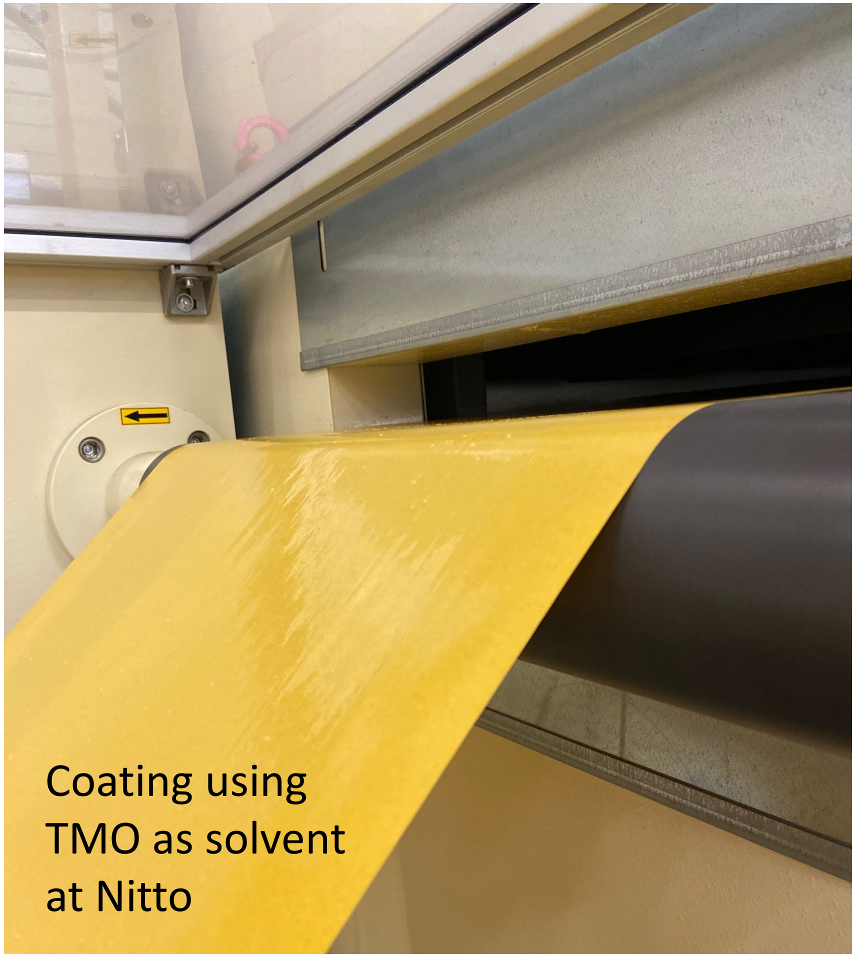
Solvent property	Toluene	Quaternary ethers: Eucalyptol	Quaternary ethers: TMO	Quaternary ethers: DTBE	THF
Boiling point / °C	111	176	112	107	66
Melting point / °C	-95	2	<-90	<-90	-108
Density / $g \cdot ml^{-1}$	0.867	0.927	0.802	0.762	0.883
Autoignition temp. / °C	522	No data	417	No data	321
Lower explosion limit / v/v%	1.1*	No data	0.9*	No data	2.0
δ_D / $MPa^{0.5}$	18.0	16.6	15.4	14.0	16.8
δ_P / $MPa^{0.5}$	1.4	2.5	2.4	2.5	5.7
δ_H / $MPa^{0.5}$	2.0	2.5	2.1	1.4	8.0
α	0.00	0.00	0.00	0.00	0.00
β	0.10	0.72	0.70	0.51	0.58
π^*	0.51	0.41	0.30	0.17	0.59
Log $P_{(o/w)}$	2.73	1.79	1.53	1.29	0.46

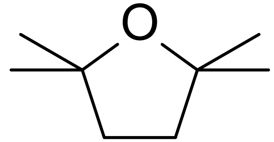


TMO

As a solvent in PSA production

- Polymer properties were almost identical when TMO was used as the solvent
  - M_w
  - M_n
  - Conversion
- PSA properties were comparable to toluene
  - Adhesion properties *better* with TMO
  - Cohesion properties worse with TMO
  - More optimisation to be done!

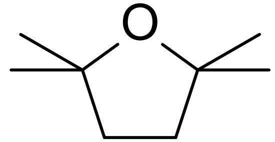




TMO

Application tests summary

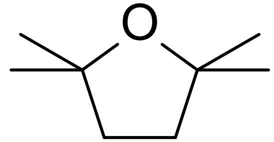
Application	Toluene-like	Ether-like
Radical-initiated polymerisation for adhesive production	✓	
Grignard reaction	✓	
Polyester synthesis	✓	
Uncatalysed esterification	✓	
Uncatalysed amidation	✓	
Buchwald-Hartwig	✓	



TMO

Toxicity

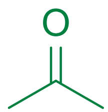
- *in vitro* testing of TMO and metabolites on a broad range of endpoints using reporter gene assays
  - No indications of (severe) toxicity ✓
  - Very similar to eucalyptol
- *in silico* analysis based on structural similarity (QSAR)
  - No indications of (severe) toxicity ✓
- Additional *in vitro* micronucleus test performed to exclude genotoxicity
  - No indications of genotoxicity ✓
- Must be extended to full testing before REACH registration



TMO

Sustainability

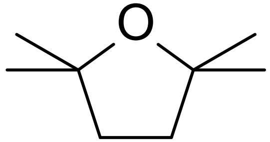
- Acetone and acetylene can be easily produced from biomass



From ABE fermentation

From Anaerobic digestion

- Superior atmospheric breakdown than toluene
  - Less polluting breakdown products
  - Likely due to quaternary carbons in structure
  - Study ongoing, publication to follow



TMO

Cost €€€

- Not commercially available at present, but research samples will be available soon

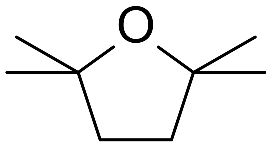
- Cost tied to *bio-based content*

  - Petroleum-derived TMO will likely be slightly more expensive than toluene
    - This is not surprising, as toluene is essentially pumped from the ground ready for use
    - However, it will be competitive

  - Increasing *bio-based content* will increase price
    - But only 25% bio-based content required to be class as bio-based (CEN/TC 411 standard)

ReSolve
SAFE AND EFFECTIVE BIO-BASED SOLVENTS

UNIVERSITY of York



TMO

Cost €€€

Positives

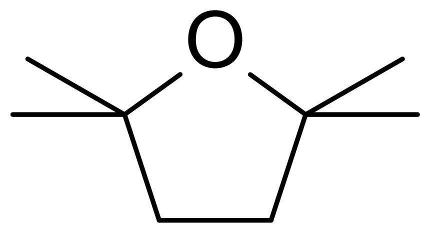
- As bio-based technology improves with increasing research, cost will come down

- Economies of scale will also see price reductions
  - Current estimates are based upon very small scale relative to toluene production

- Contact me for research samples!

Addible.co.uk

2,2,5,5-Tetramethyloxolane (TMO)



Green solvent requirements

Easy to synthesise	✓	*4 steps from biomass*
Safe	✓	*Non-toxic, non-peroxide forming in storage conditions*
Easy to remove	✓	*But not too easy to remove*
Low-polarity	✓	*Not necessarily exact replica of traditional hydrocarbons*
High-performance	✓	*Must not interfere with product formation*
Sustainable	✓	*The use of biomass waste*
Cost efficient	✓	*Will compete with petrochemicals*

Special thanks to

Bio-Based Industries Joint-Undertaking (BBI JU)

Nitto Belgium

Bio-Based Europe Pilot Plant (BBEPP)

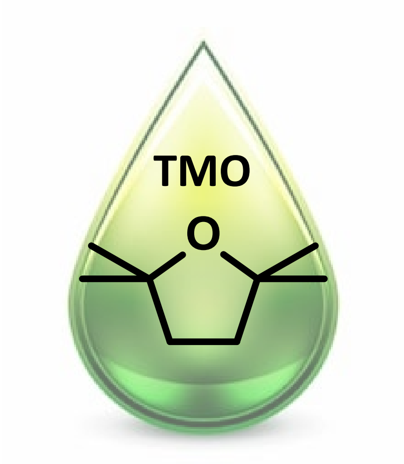
BioDetection Systems (BDS)

Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek (TNO)

University of York

Thanks for listening!

Any questions?

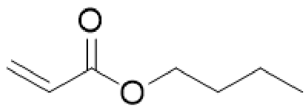


2,2,5,5-Tetramethyloxolane (TMO)

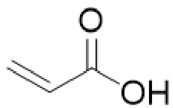
Application testing

- Radical-initiated polymerisation

Patented by Nitto
WO2018033634 (A1)



Butyl acrylate
100 g



Acrylic acid
5 g

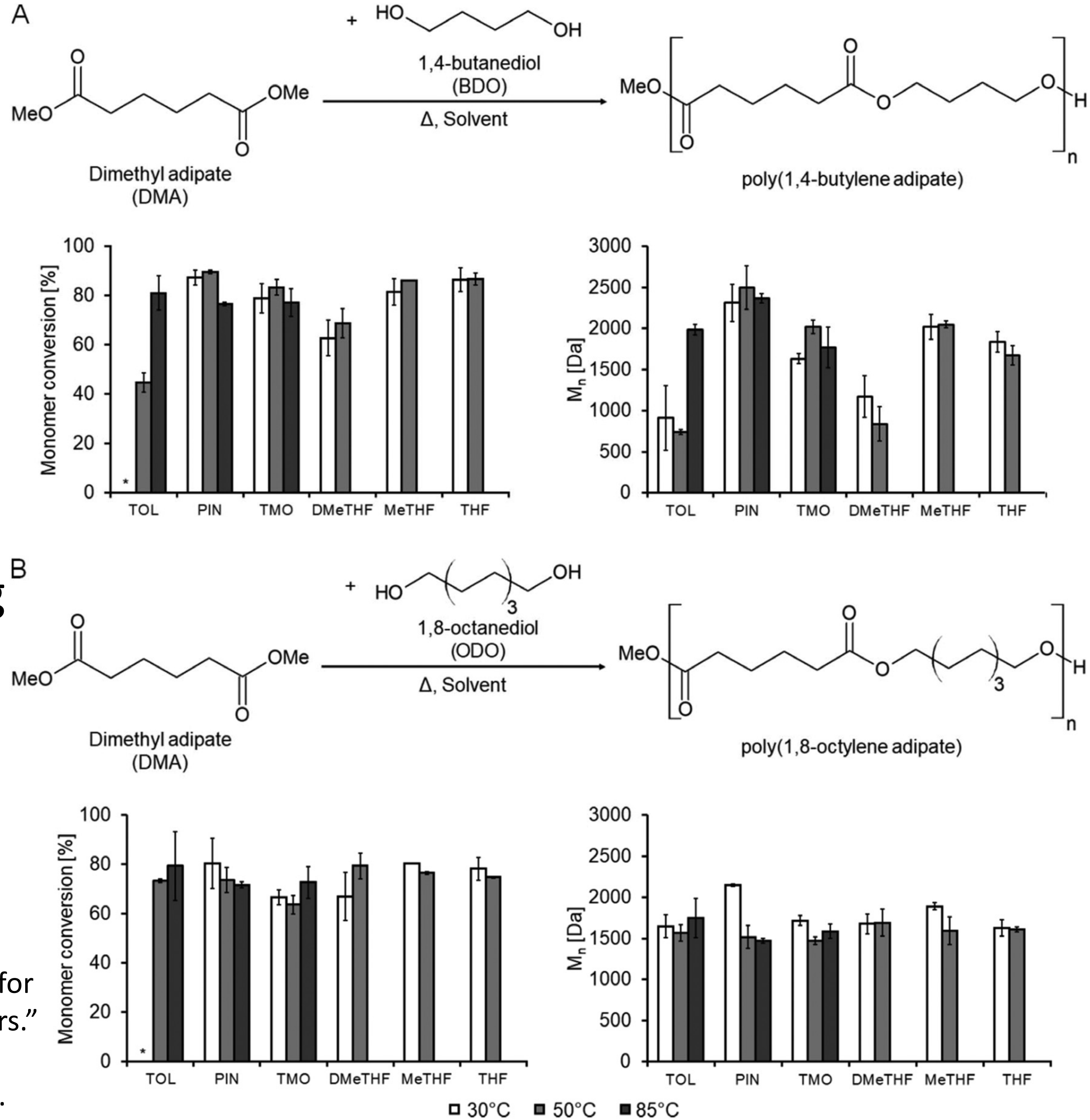
Polymer property	TMTHF	Toluene	2-MeTHF
Mw / g·mol^{-1} (a)	501,000	509,000	9200
Solid content / % (b)	27.25	31.00	31.00
Adhesion / cN·20mm^{-1} (c)	809	757	n/a (f)
Cohesion / days (d)	>10	>10	n/a (f)
Tack (wt supported) / g (e)	291	264	n/a (f)

F. Byrne, B. Forier, G. Bossaert, C. Hoebers, T. J. Farmer, J. H. Clark, and A. J. Hunt. "2,2,5,5-Tetramethyltetrahydrofuran (TMTHF): A Non-Polar, Non-Peroxide Forming Ether Replacement for Hazardous Hydrocarbon Solvents." *Green Chemistry* 19, 3671–78. https://doi.org/10.1039/C7GC01392B.

2,2,5,5-Tetramethyl oxolane (TMO)

Application testing

- Polyester synthesis

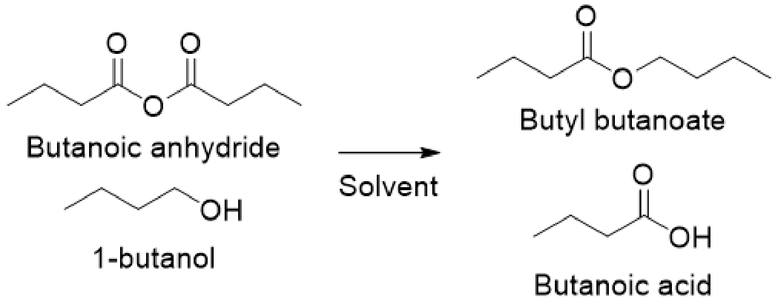


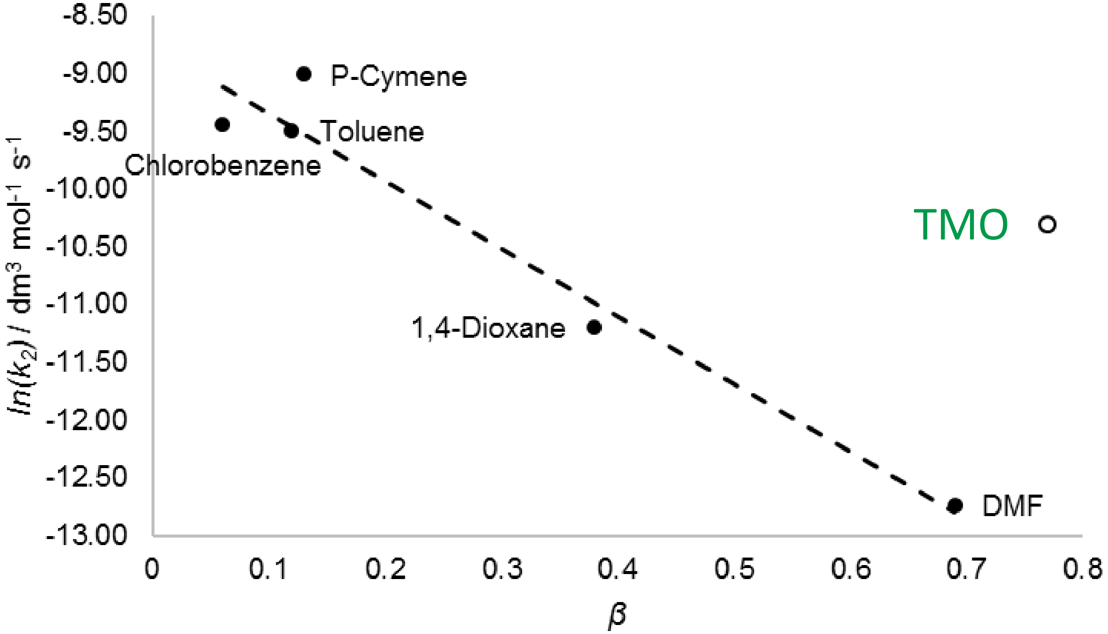
A. Pellis, F. P. Byrne, J. Sherwood, M. Vastano, J. W. Comerford, and T. J. Farmer. "Safer Bio-Based Solvents to Replace Toluene and Tetrahydrofuran for the Biocatalyzed Synthesis of Polyesters." *Green Chemistry*, https://doi.org/10.1039/C8GC03567A.

2,2,5,5-Tetramethyloxolane (TMO)

Application testing

- Uncatalysed esterification

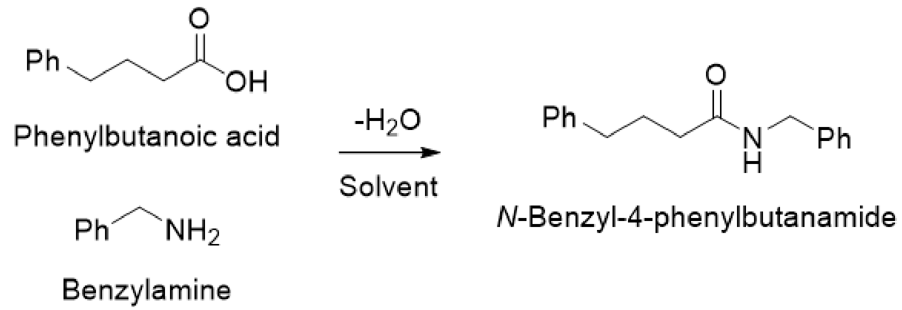


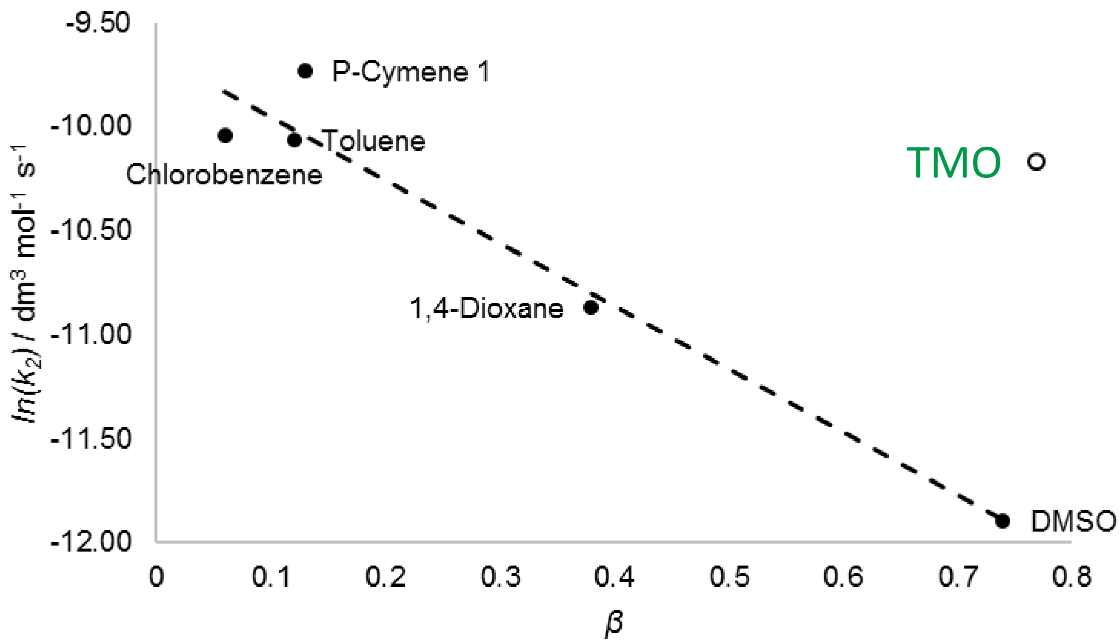


2,2,5,5-Tetramethyloxolane (TMO)

Application testing

- Uncatalysed amidation

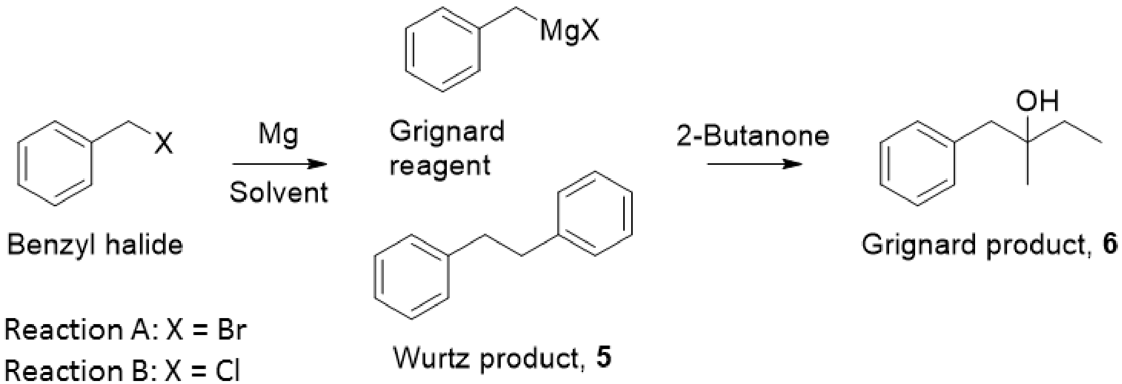




2,2,5,5-Tetramethyloxolane (TMO)

Application testing

- Radical-initiated polymerisation

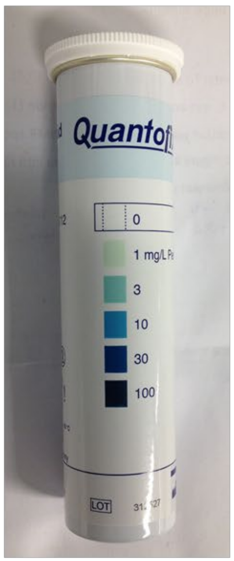


Reaction A: X = Br
Reaction B: X = Cl

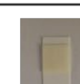
	Reaction A		Reaction B	
Solvent	Conv. alkyl halide (%)	Ratio **6**:**5**	Conv. alkyl halide (%)	Ratio **6**:**5**
THF	99	82:18	99	67:33
2-MeTHF	100	87:13	100	97:3
TMTHF	0	-	0	-
Toluene	0	-	0	-

2,2,5,5-Tetramethyloxolane (TMO)

Peroxide test



Scale

Solvent		T = 0 hours (ppm)		T = 3 hours (ppm)	
THF	Control		10-30		10-30
	Test		10-30		>100
2-MeTHF	Control		2		2
	Test		2		>30
CPME	Control		1		1
	Test		1		3-10
TMTHF	Control		0		0
	Test		0	 0 	0 (reflux)