BAGKF

Metathese in der Oleochemie

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- ehemals -

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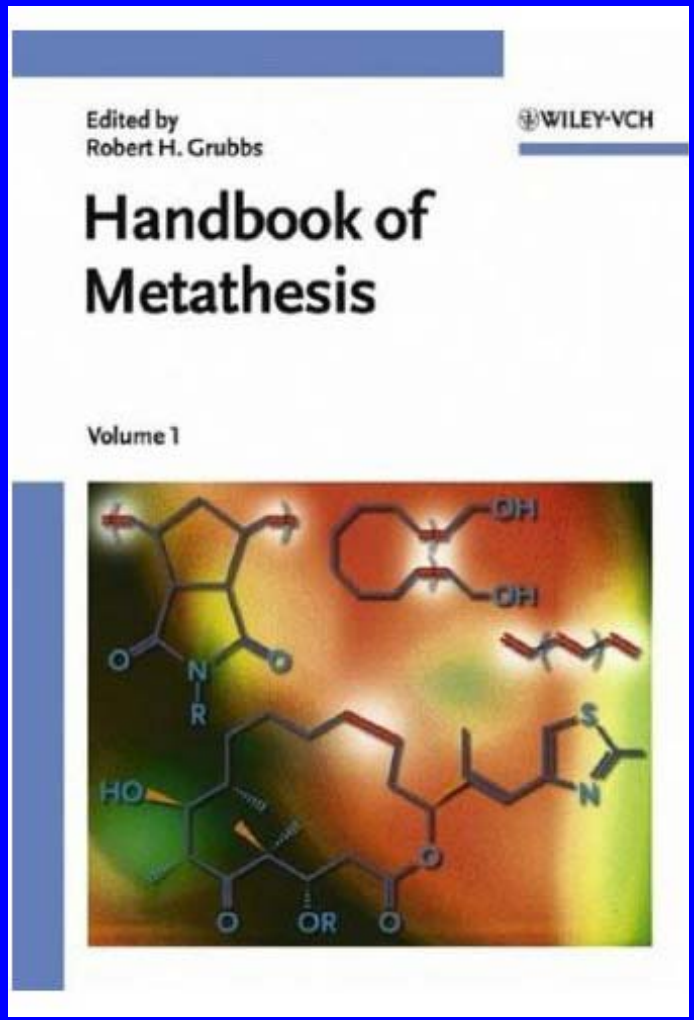
Bundesanstalt für Getreide-, Kartoffel- und Fettforschung,

Münster

Metathesis



2003 Volume 1-3

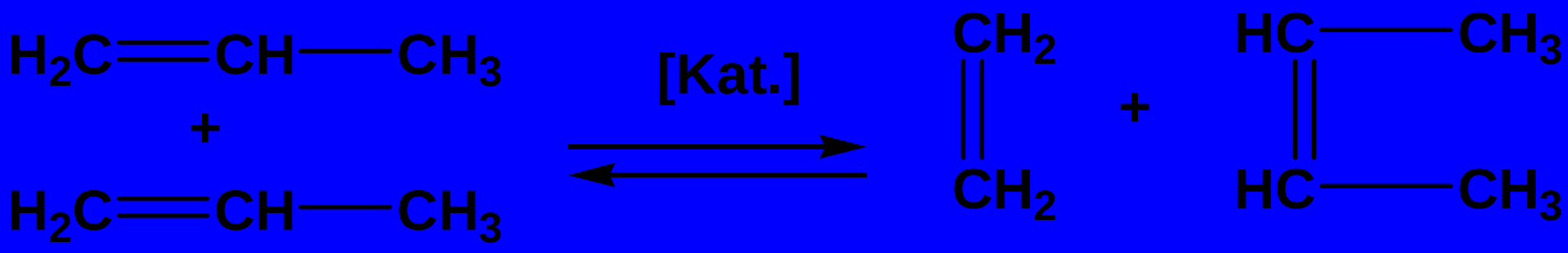
Chemie – Nobelpreis 2005

Y. Chauvin

R.H. Grubbs

R.R. Schrock

Phillips – Triolefin – Prozess



50% 50%

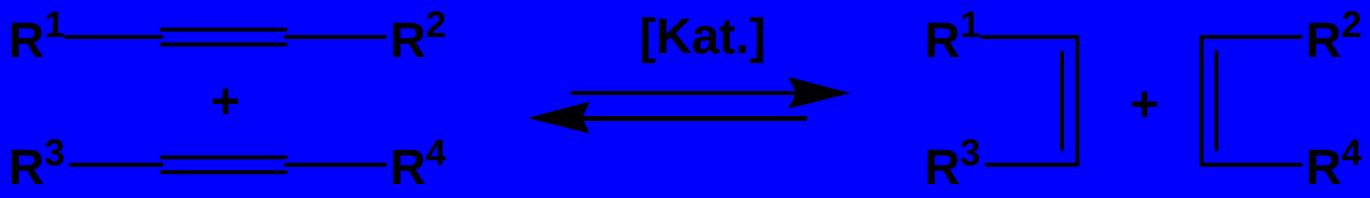
Co-MoO_3 / Al_2O_3 bei 150°C; WO_3 / SiO_2 bei 300°C

R.L. Blanks und G.C. Bailey,

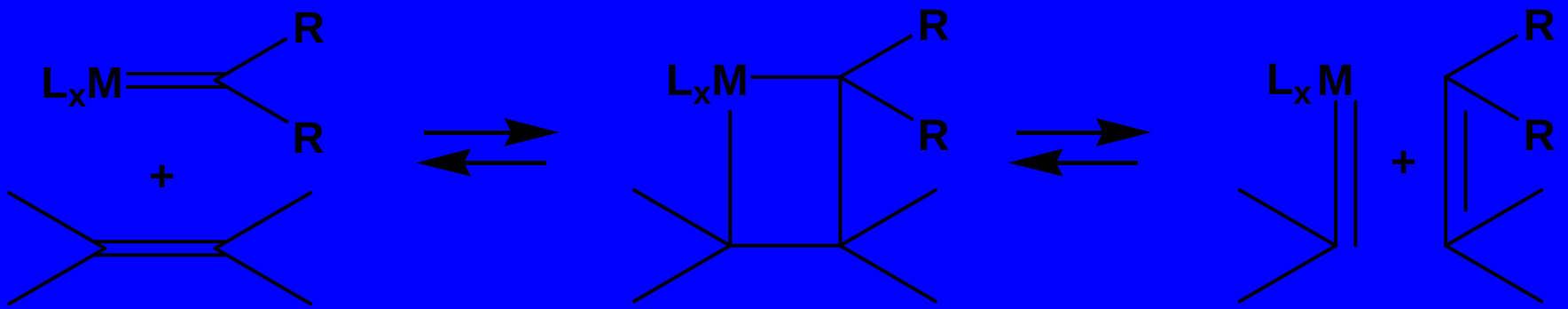
Ind. Eng. Chem. Prod. Res. Develop. 3, 170 (1960)

Olefin-Metathese

Reaktionsmuster



Mechanismus



Katalysatoren

heterogen

Re_2O_7 / Al_2O_3

$CoO\text{-}MoO_3$ / Al_2O_3

WO_3 / SiO_2

homogen

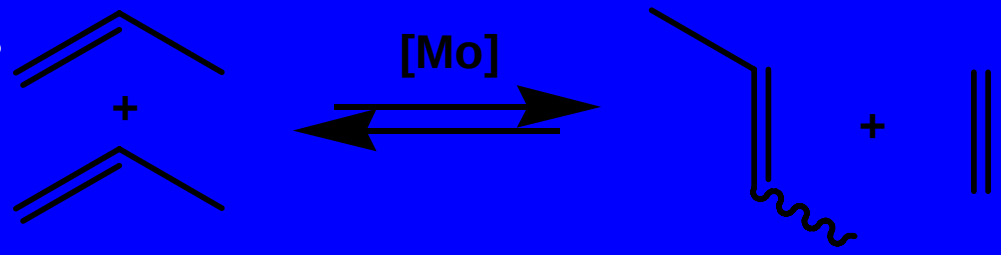
$MoCl_2(NO)_2(PR_3)_2/RAlCl_2$

WCl_6 / EtOH / $EtAlCl_2$

WCl_6 / Et_2O / SnR_4

Industrielle Anwendungen

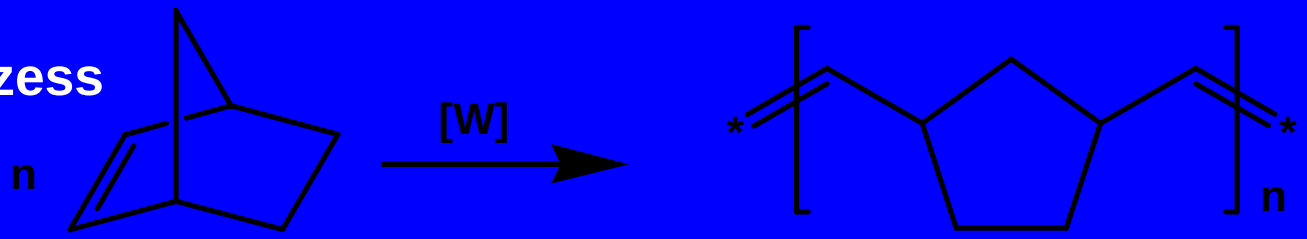
A) Phillips – Triolefin – Prozess



B) Shell – Higher – Olefin – Prozess (SHOP)

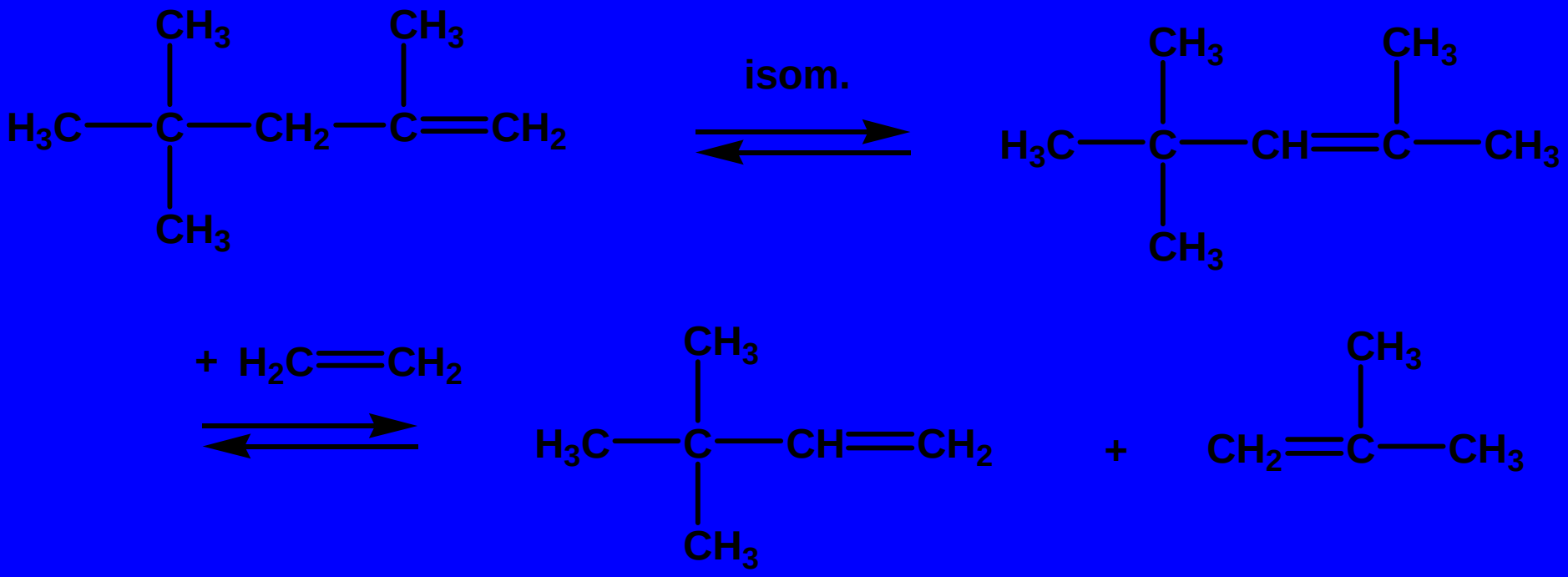
Kurzkettige Olefine
\+
Langkettige Olefine
⟷ olefine mttlerer Länge (C11-C14)

C) Norsorex – Prozess



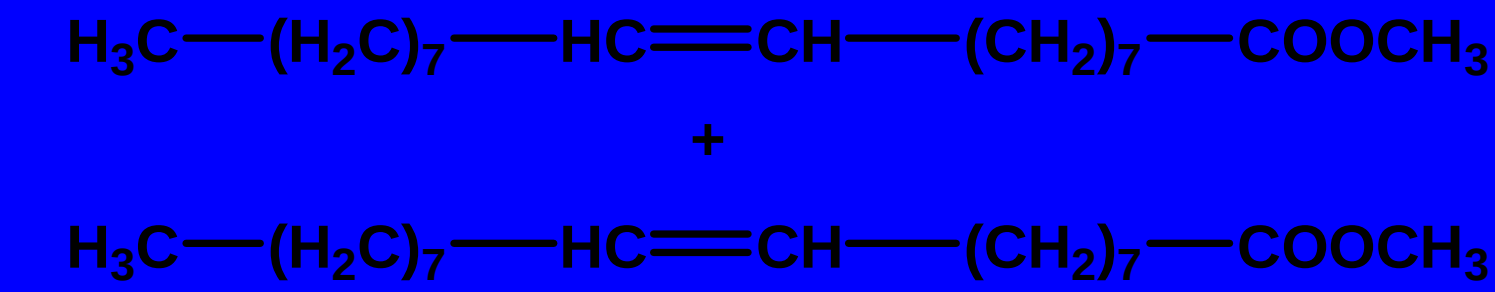
D) Hüls – Vestenamer – Verfahren

Neohexen – Prozess

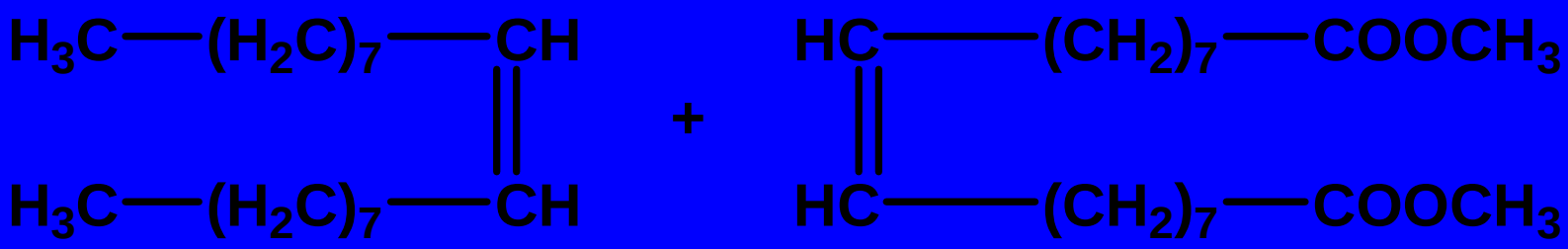


Kat.: WO_3 / SiO_2 + MgO; 370°C

Metathese von Ölsäuremethylester



50%



50%

C. Boelhouwer et al., Chem. Commun. 1972, 1221

Katalysatoren
für die Metathese unges. Fettsäureester

konventionell:

WCl_6 / $SnMe_4$	(C. Boelhouwer et al.)
Re_2O_7 / Al_2O_3 + $SnMe_4$	(C. Boelhouwer, J.C. Mol et al.)
CH_3ReO_3 + Al_2O_3	(W.A. Herrmann et al.)

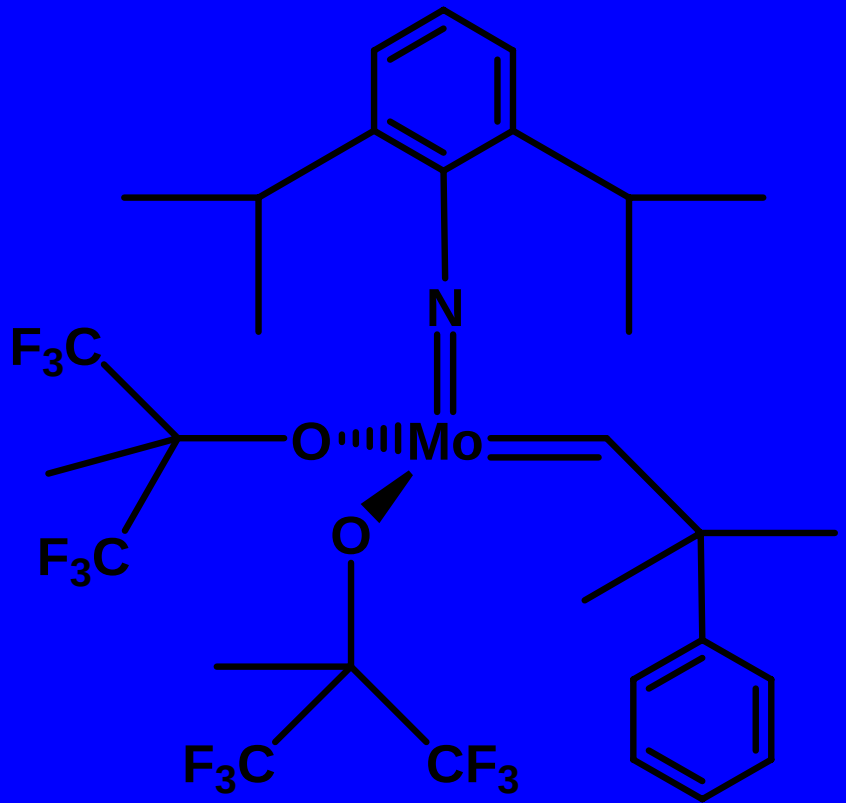
neu:

Re_2O_7 - B_2O_3 / Al_2O_3 – SiO_2 + $SnMe_4$

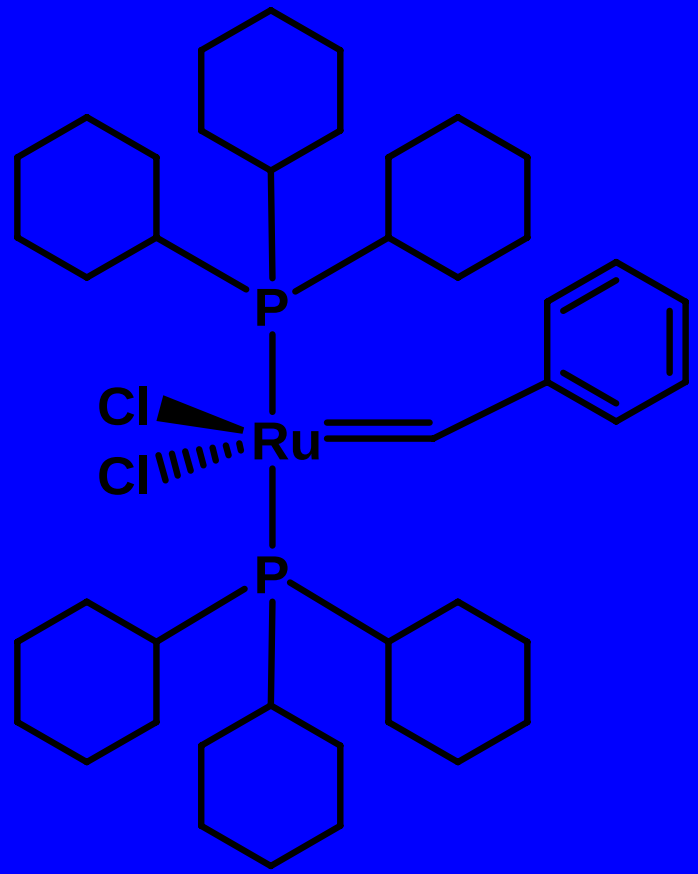
CH_3ReO_3 + B_2O_3 - Al_2O_3 - SiO_2

Al_2O_3 - SiO_2 : amorphe Aluminosilikate

Metallcarbene als homogene Ein-Komponenten-Katalysatoren für die Olefin - Metathese

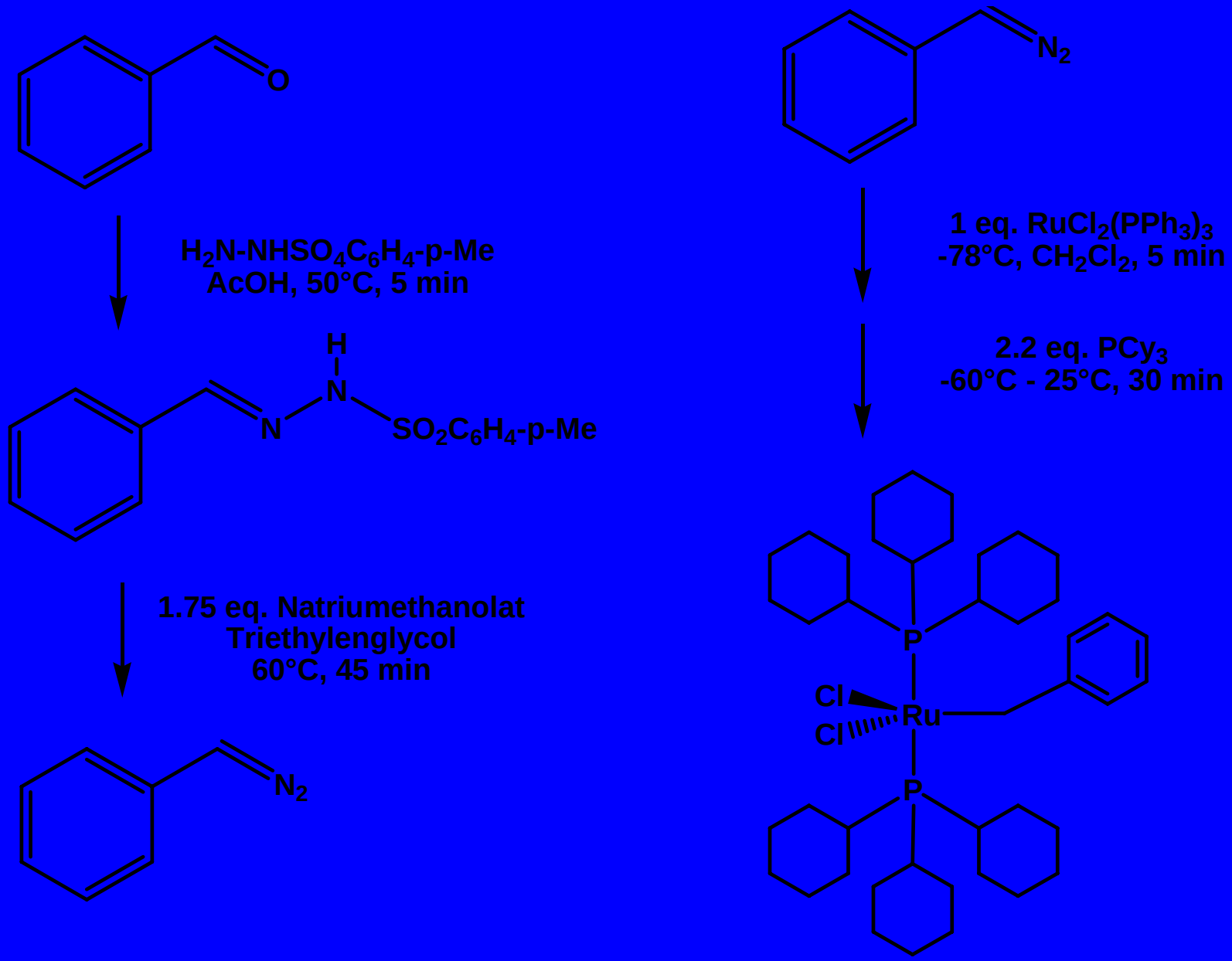


R. Schrock

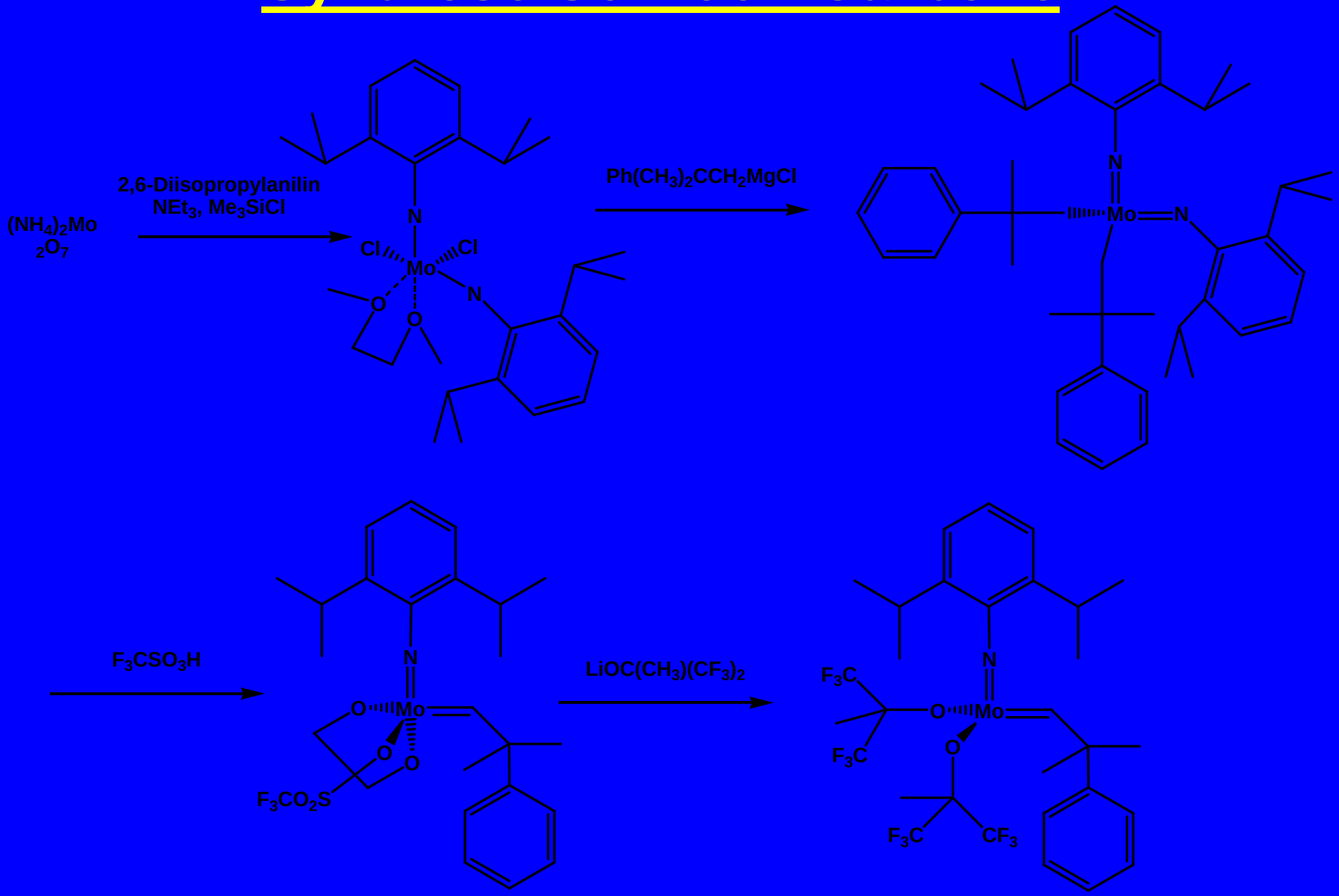


R.H. Grubbs

Synthese von RuCl2(=CHPh)(PCy3)2



Synthese Schrock-Carbene



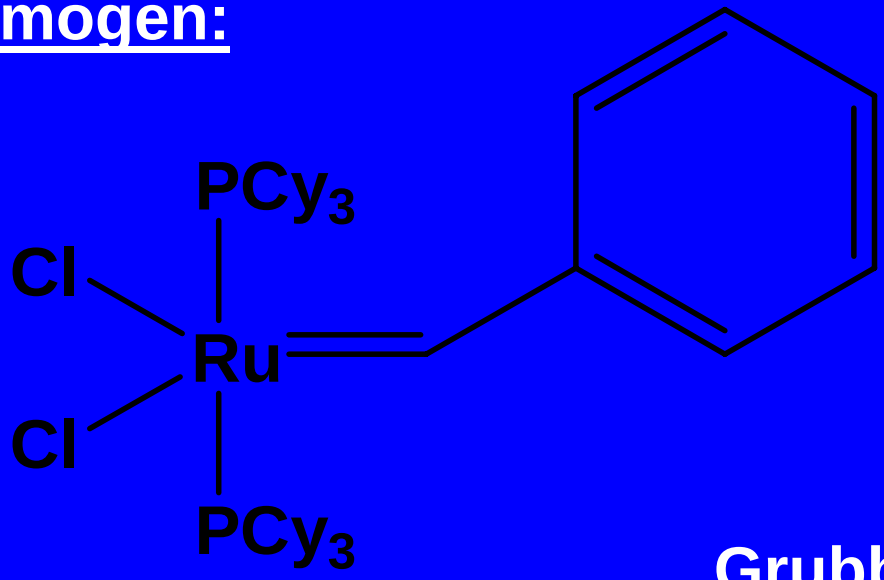
Metathese - Katalysatoren

Heterogen:

Re_2O_7 / B_2O_3 - Al_2O_3 + $SnMe_4$

CH_3ReO_3 + B_2O_3 - Al_2O_3 - SiO_2

Homogen:

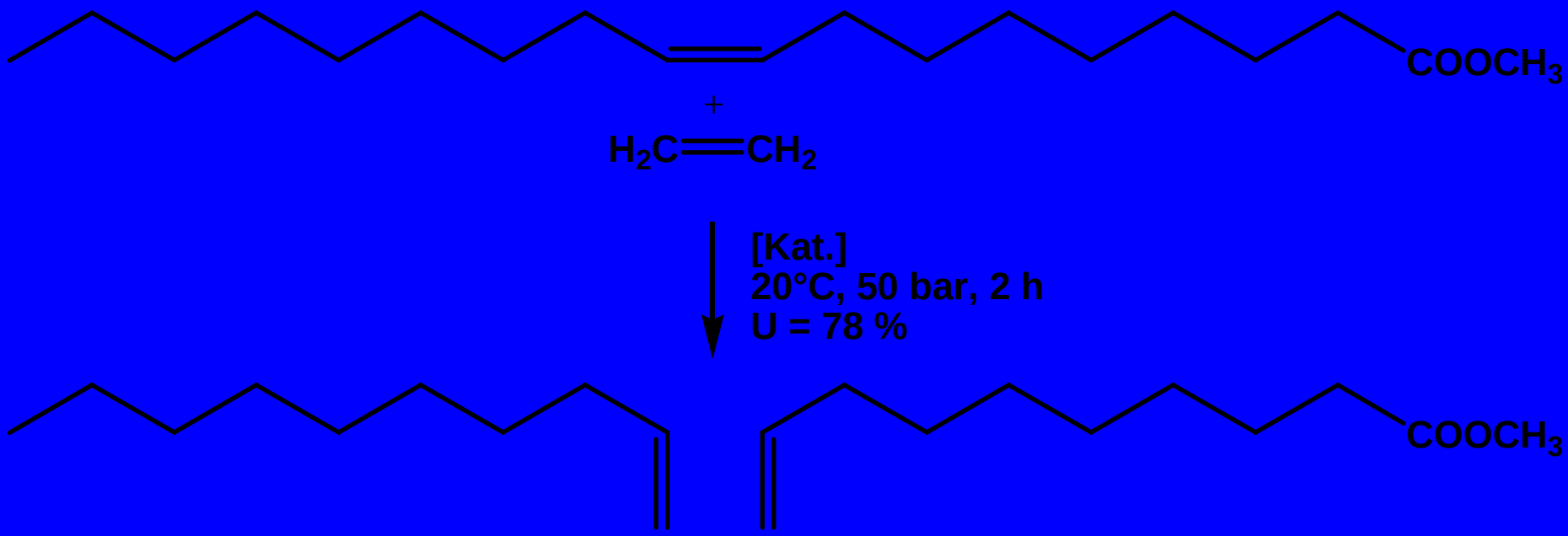


Grubbs - Katalysator

Metathese – Reaktionen von Fettsäurestern

- Kettenveränderung mit symmetrischen Olefinen
- Ethenolyse
- metathetische Kondensation
- metathetische Polykondensation

Metathese von Ölsäuremethylester mit Ethylen an heterogenen Rheniumoxid-Katalysatoren



Edukt: 87%ig aus ölsäurereichem Sonnenblumenöl

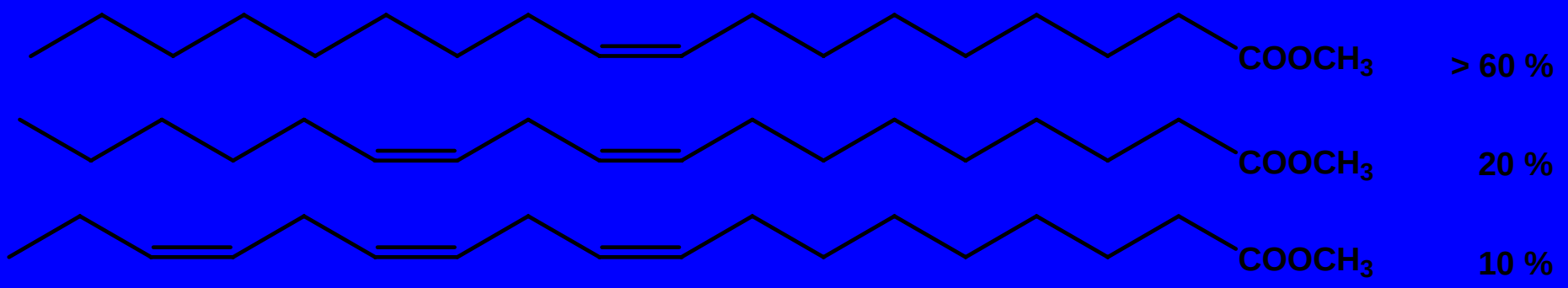
Katalysatoren B_2O_3 - Re_2O_7 / Al_2O_3 - SiO_2 + $SnMe_4$

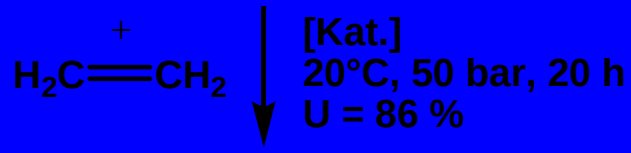
CH_3ReO_3 + B_2O_3 - Al_2O_3 - SiO_2

Re_2O_7 / + $SnBu_4$ / Ester = 1 / 1,5 / 600 (molar)

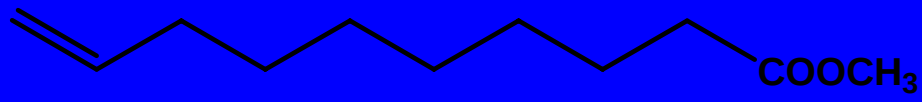
Ausbeuten an 9 Decensäuremethylester: > 80 % (nach Destillation)

Metathese von RME („Biodiesel“) mit Ethylen



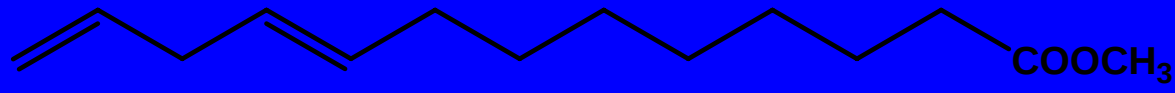


C10:



89.5 %

C13:



7.5 %

sonstige ungesättigte Ester 3.0 %

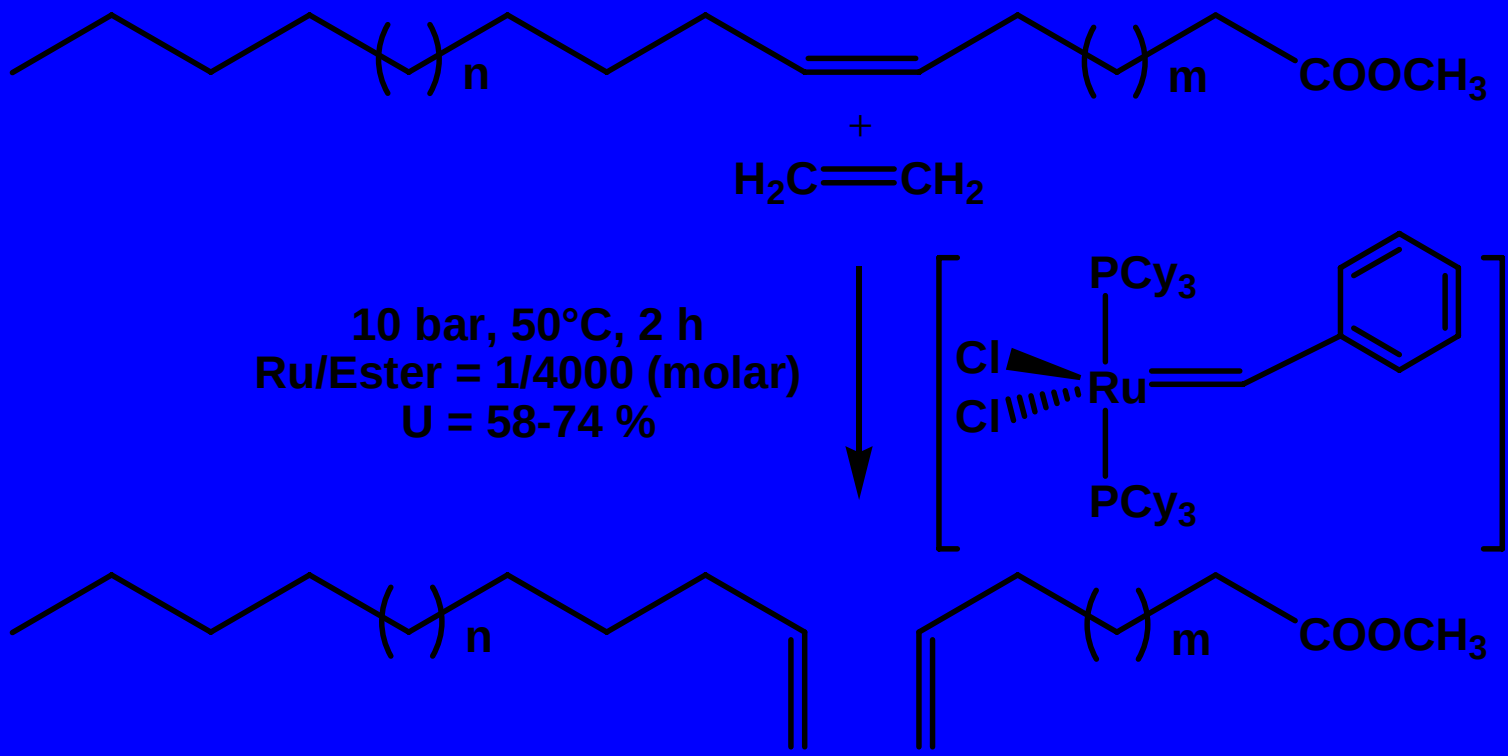
Reaktoren zur Metathese

- **Batch - Druckreaktoren**
- **Airlift - Schlaufenreaktor**
- **Kontinuierliche Reaktoren**

Ungesättigte Fettsäuren in Pflanzenölen

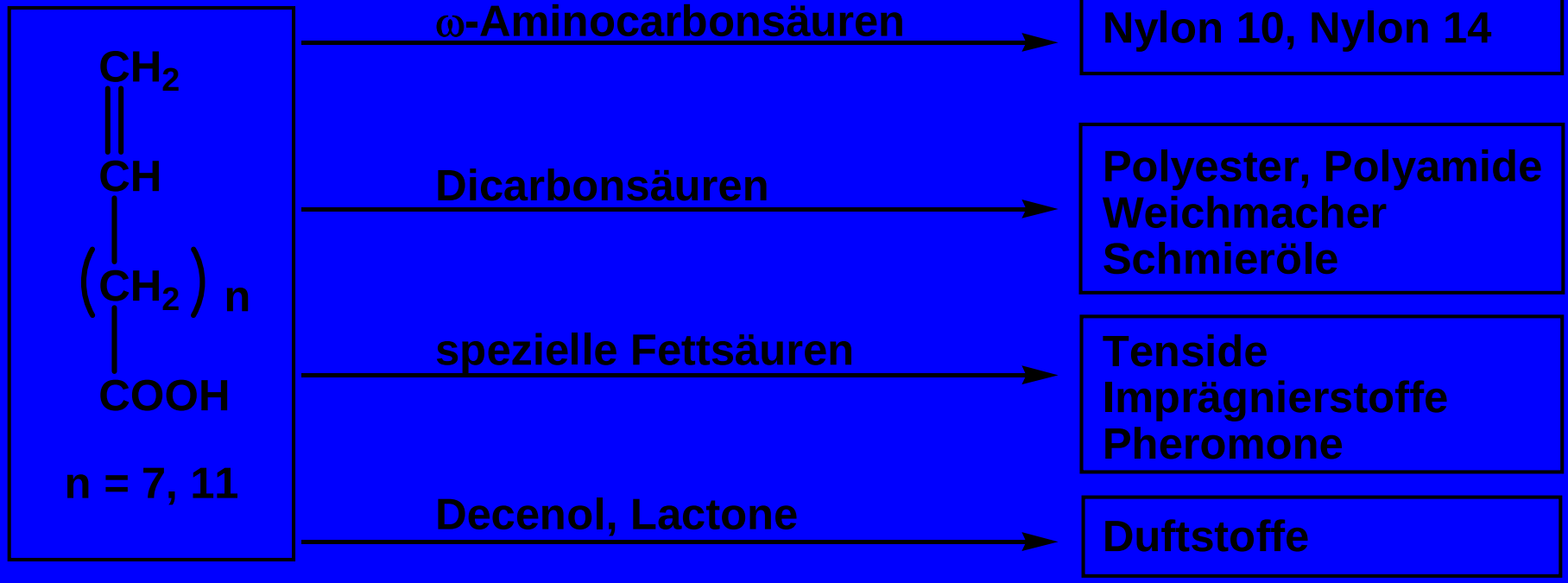
Pflanzenöl	Hauptfettsäure	Anteil (%)
Sonnenblumenöl (hochölsäurereich)	Ölsäure C18:1-Δ9	86
00-Rapsöl	Ölsäure C18:1-Δ9	63
Korianderöl	Petroselinsäure C18:1-Δ6	75
Meadowfoam - Öl	5-Eicosensäure C20:1-Δ5	63
Rapsöl (erucasäurereich)	Erucasäure C22:1-Δ13	48
Crambe - Öl	Erucaäure C22:1-Δ13	59

Metathese ungesättigter Fettsäuremethylester mit Ethylen mittels homogener Ruthenium - Katalysatoren

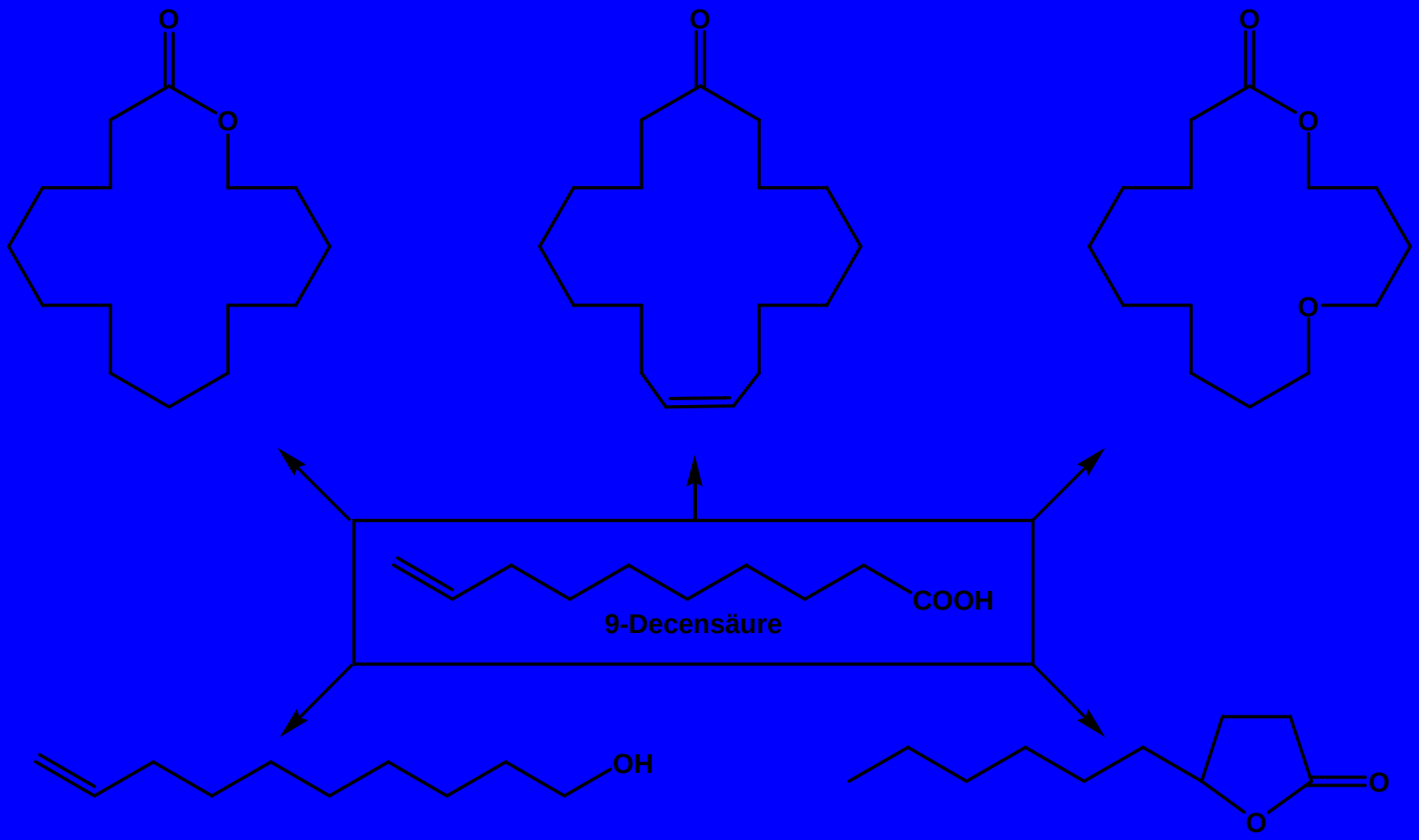


m = 1, n = 7:	5-Eicosensäure-ME	⇒	5-Hexensäure-ME
m = 2, n = 4:	Petroselinsäure-ME	⇒	6-Heptensäure-ME
m = 5, n = 1:	Ölsäure-ME	⇒	9-Decensäure-ME
m = 9, n = 1:	Erucasäure-ME	⇒	13-Tetradecensäure-ME

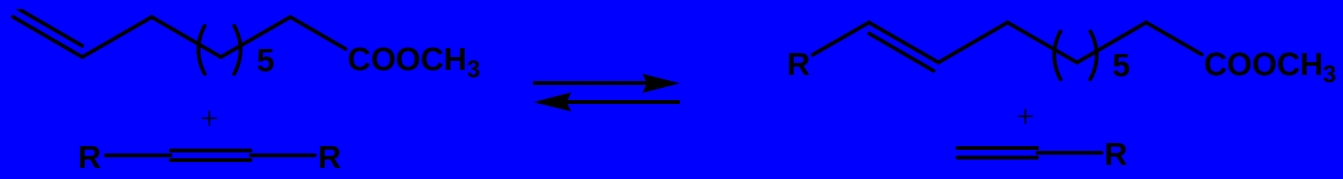
Anwendungspotential von 9-Decensäure und 13-Tetradecensäure



Duftstoffe auf Basis von 9-Decensäure



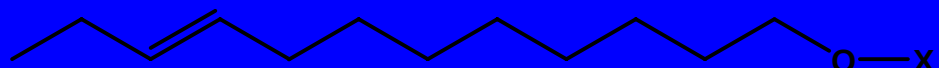
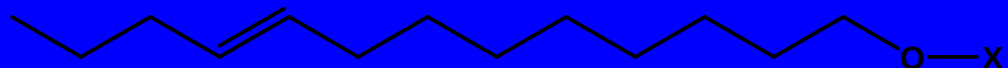
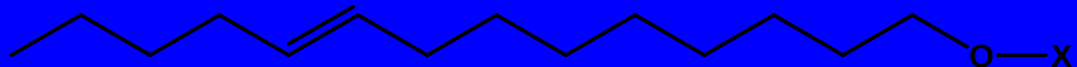
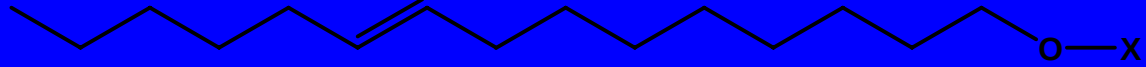
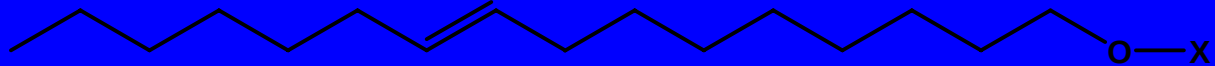
Insektenpheromone auf Basis von 9-Decensäuremethylester



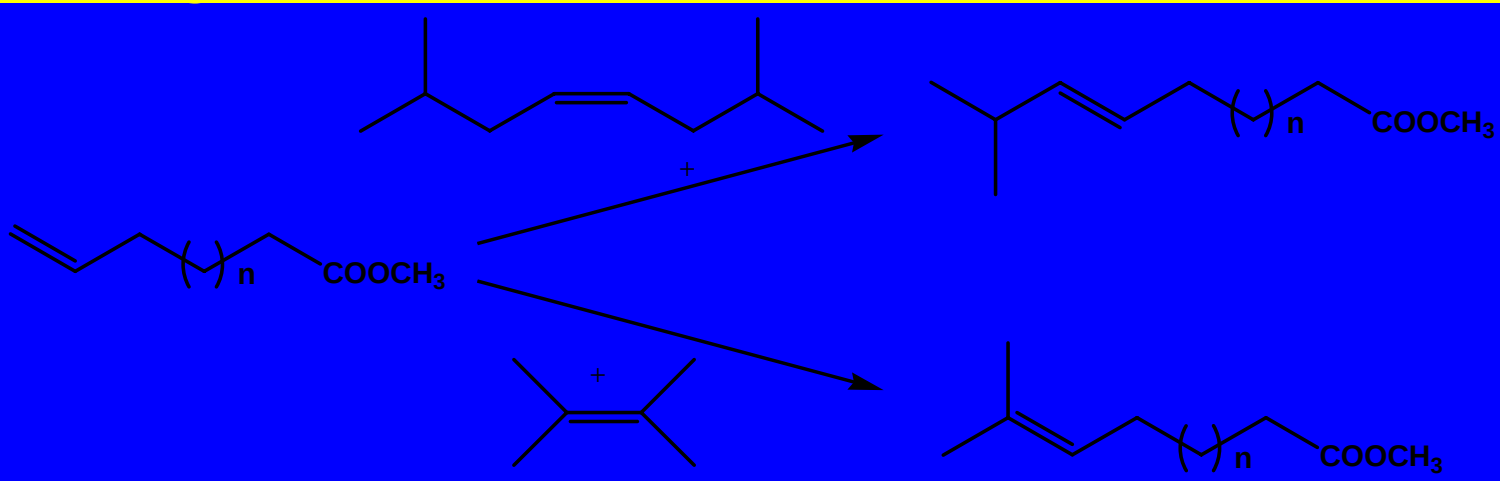
Olefin: 3-Hexen, 4-Octen, 5-Decen, 6-Dodecen, 7-Tetradecen

Kat.: B_2O_3-Re_2O_7 / Al_2O_3-SiO_2 + $SnBu_4$; 20°C, 5 h; Re_2O_7 / $SnBu_4$ / Ester / Olefin = 1 / 1,5 / 1200 / 2400 (molar)

Umsätze: 78-85 %; Co-Metathese 85-89 %

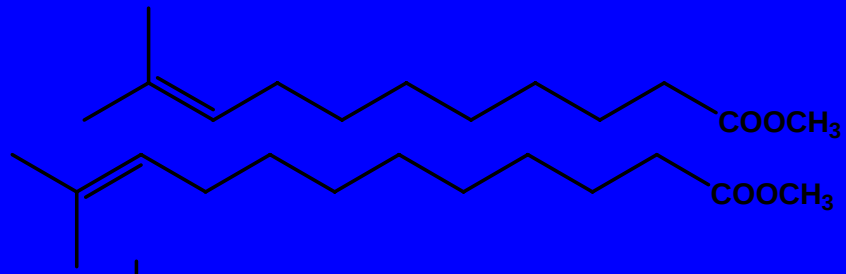
	Pheromon	Insekt
C12		Eucosma sonomana (western pine shoot borer) -Forst- Eupoecilia ambiguella (Einbindiger Traubenwickler) -Weinbau-
C13		Pammene rhediella Bodenseewickler -Obstplantagen-
C14		z.B. Spodoptera littoralis -Baumwolle- Ostrinia nubilalis -Mais-
C15		Acrobasis rufimbalis
C16		Heliothis zea -Getreide-

Verzweigte Fettsäureester durch Olefin Metathese



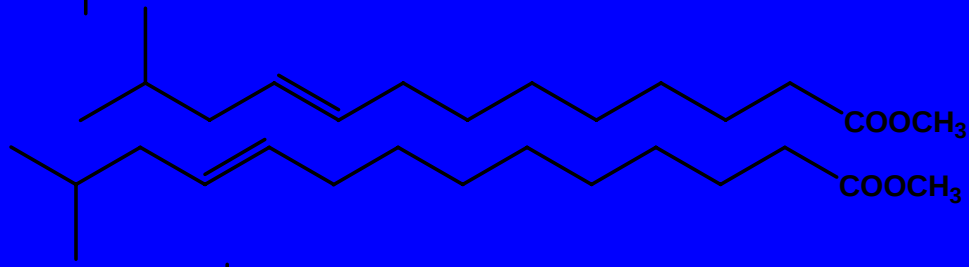
C12; (C10 + A)

C13; (C11 + A)



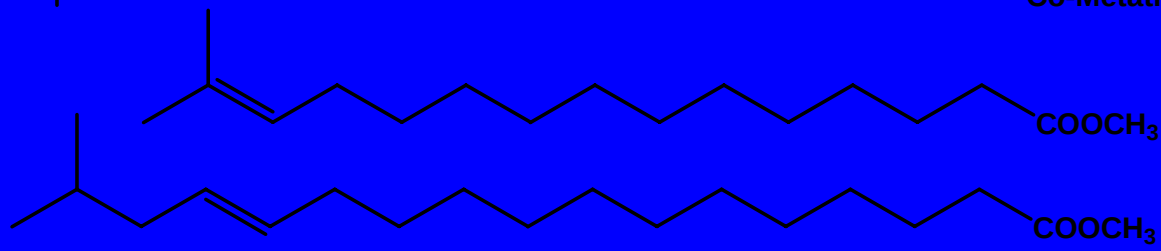
C14; (C10 + B)

C15; (C11 + B)



C16; (C14 + A)

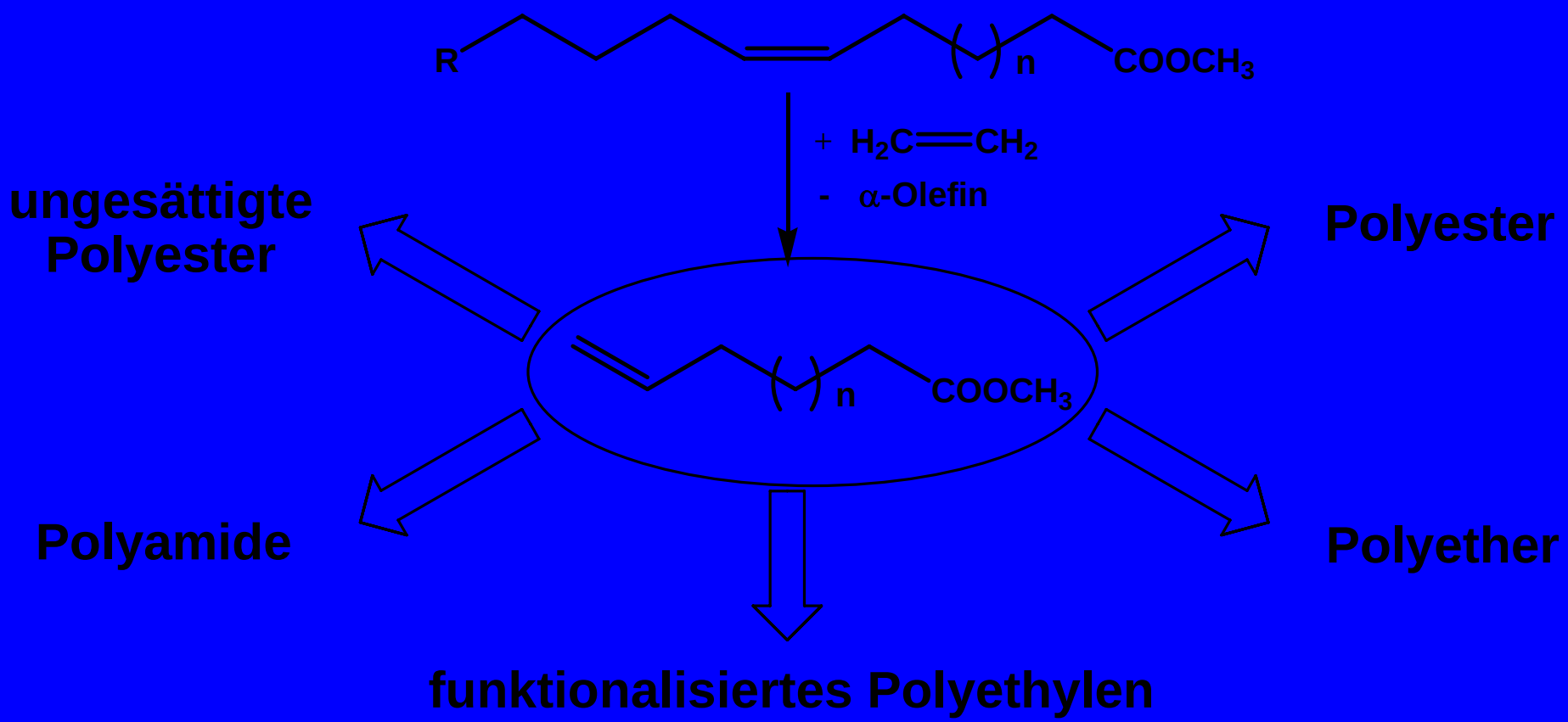
C18; (C14 + B)



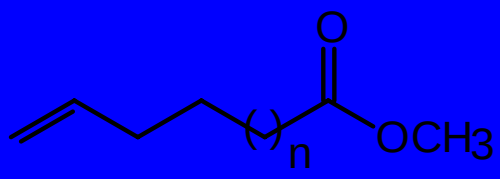
A: 2,3-Dimethyl-2-buten;
B: 2,7-Dimethyl-4octen,
C10: 9-Decensäure,
C11: 10-Undecensäure,
C14: 13-Tetradecensäure,

Kat.: B_2O_3-Re_2O_7 / Al_2O_3-SiO_2 + $SnBu_4$;
50°C, 2 h;
Umsätze: 80-97 %;
Co-Metathese 70-75 %

Endständig ungesättigte FSME und Derivate



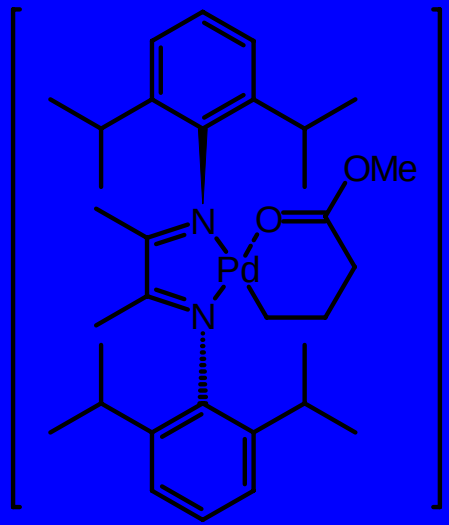
Co-polymerisation von Ethylen mit ω-ungesättigten Fettsäuremethylestern

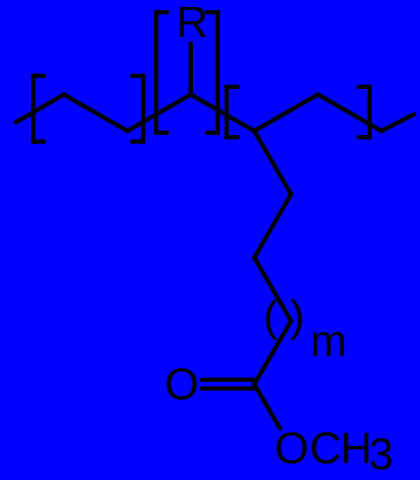


n = 1,2,5,6,9

2,5 bar $H_2C=CH_2$

CH_2Cl_2, 25 °C, 18 h



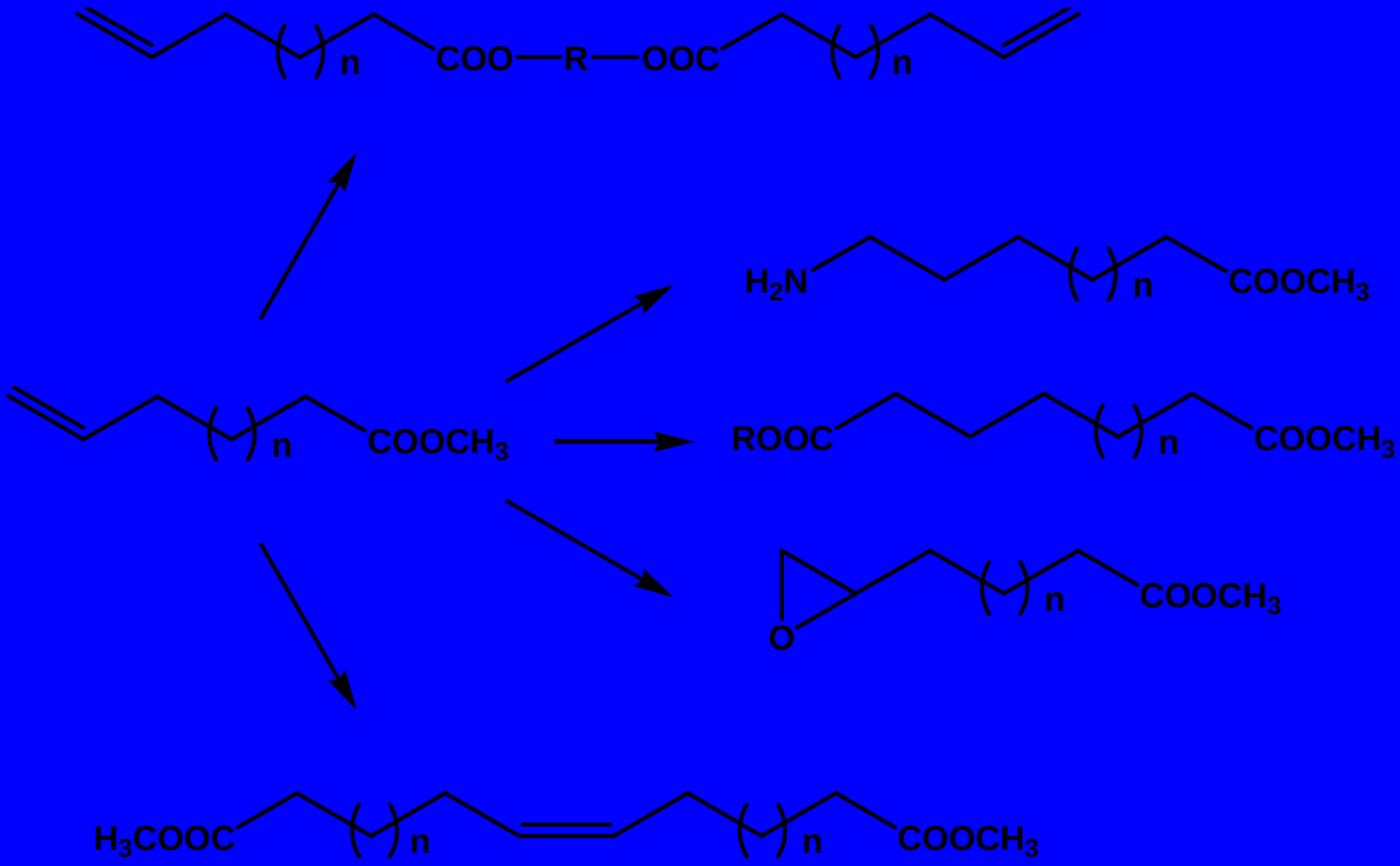


verzweigtes, funktionalisiertes Polyethylen

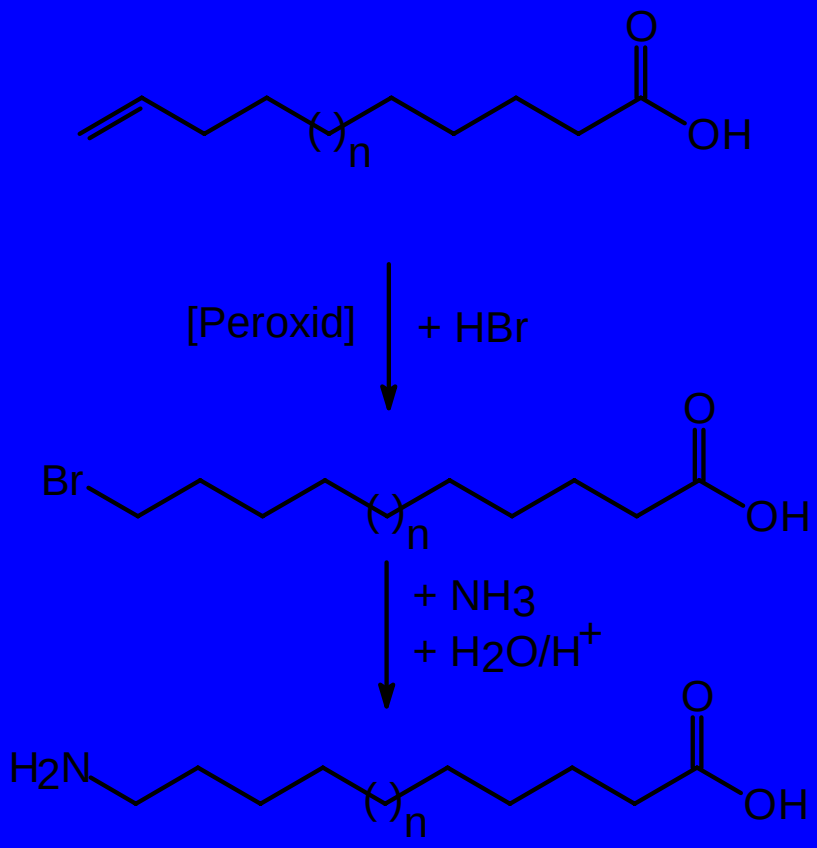
M_W : 90.000-200.000 g/mol

max. Inkorporation Ester: 15 Gew-%

Polymer - Bausteine

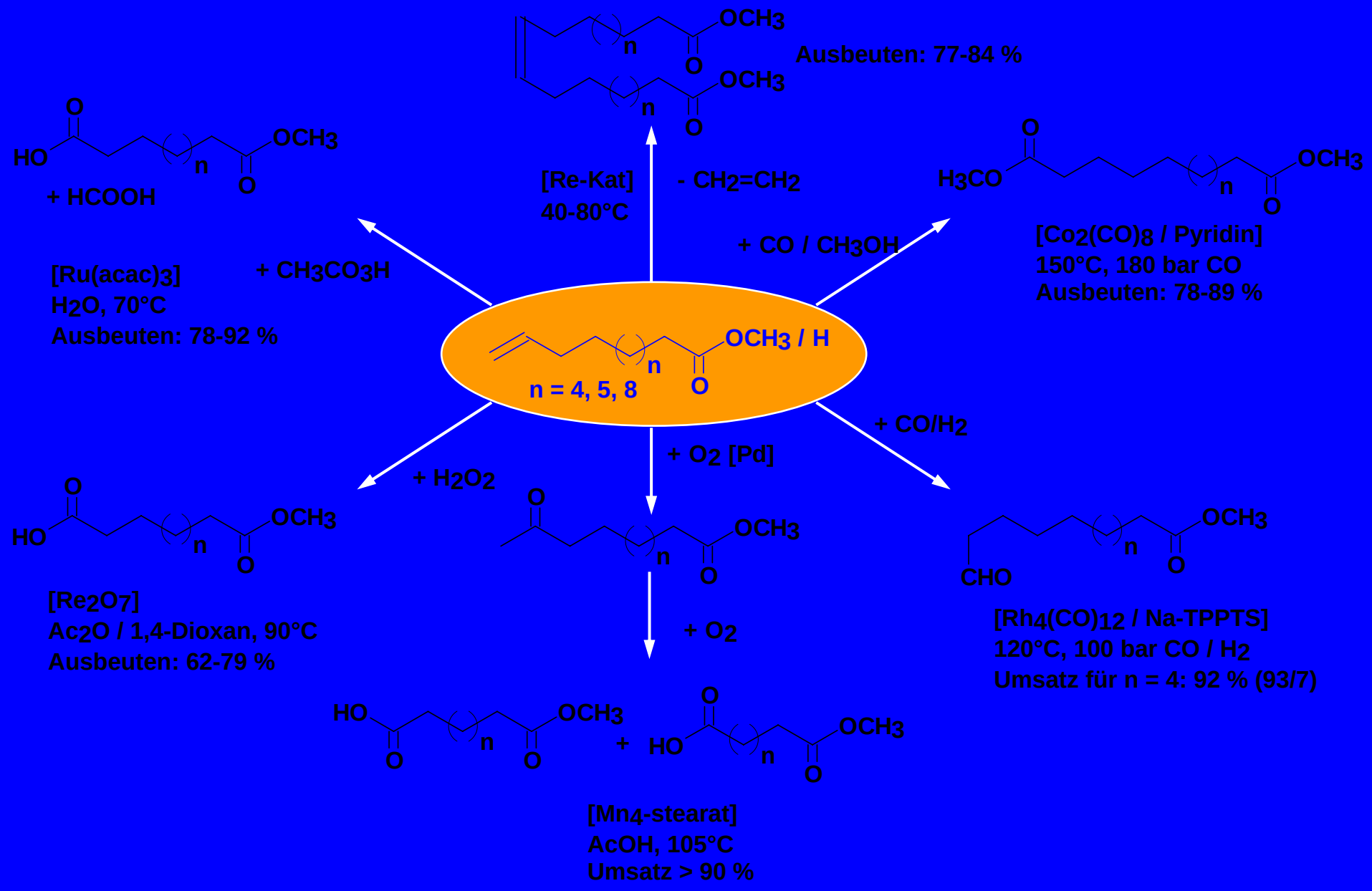


ω-Aminocarbonsäuren

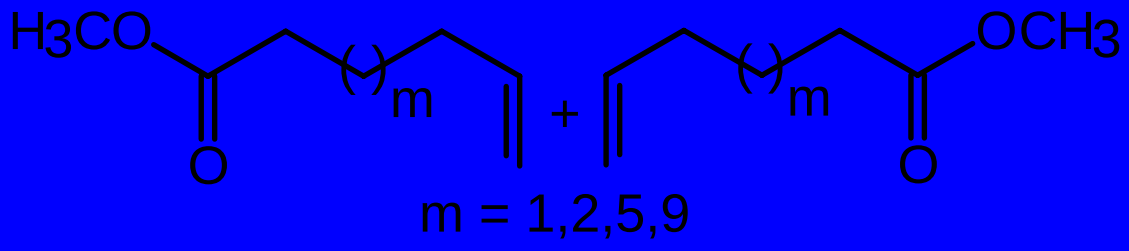


5-Hexensäure	→	Nylon 6
6-Heptensäure	→	Nylon 7
9-Decensäure	→	Nylon 10
10-Undecensäure	→	Nylon 11 (Rilsan)
13-Tetradecensäure	→	Nylon 14

Dicarbonsäuren aus ω-ungesättigten Fettsäureestern



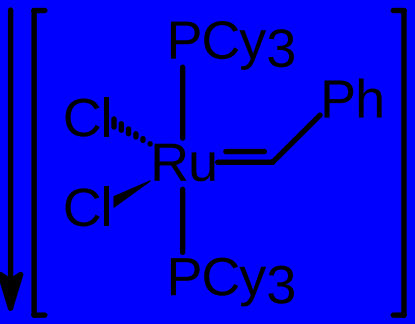
Metathetische Kondensation ungesättigter Fettsäureester

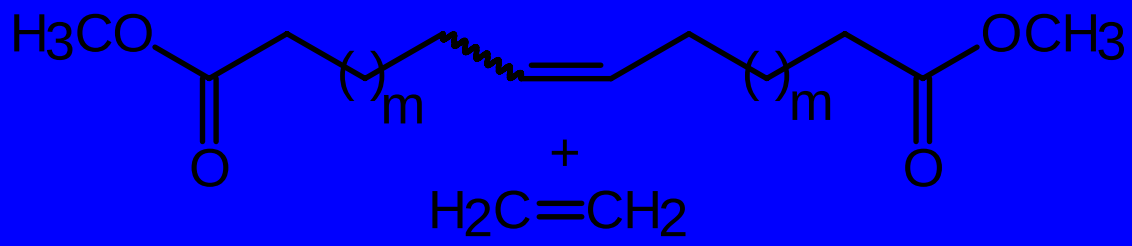


50°C, 2h, Vakuum

Ru/Ester = 1/10.000

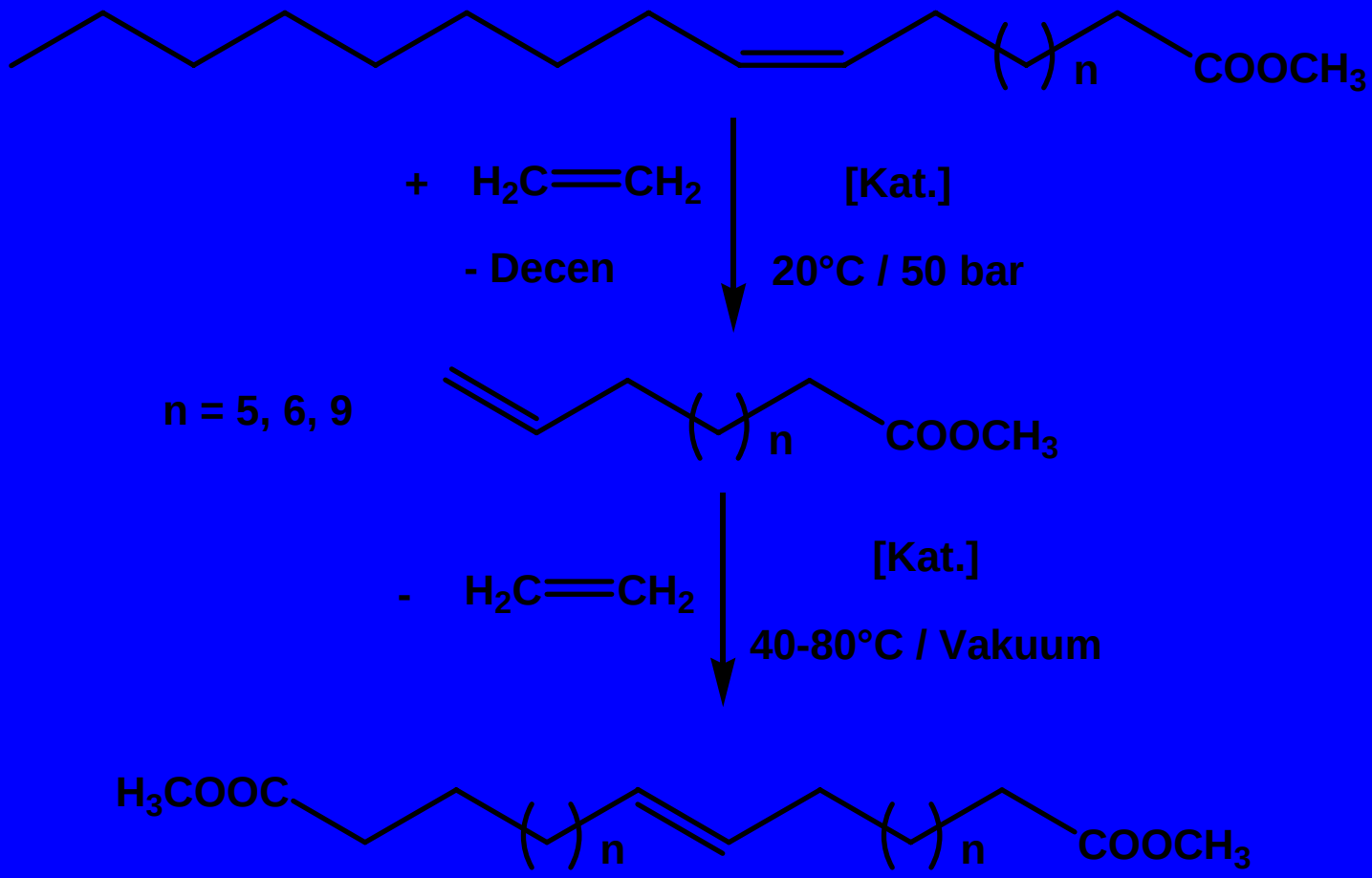
U = 74-82%





5-Hexensäureester	→	C_{10}-Dicarbonsäureester
6-Heptensäureester	→	C_{12}-Dicarbonsäureester
9-Decensäureester	→	C_{18}-Dicarbonsäureester
10-Undecensäureester	→	C_{20}-Dicarbonsäureester
13-Tetradecensäureester	→	C_{26}-Dicarbonsäureester

Langkettige, ungesättigte Dicarbonsäureester durch metathetische Kondensation



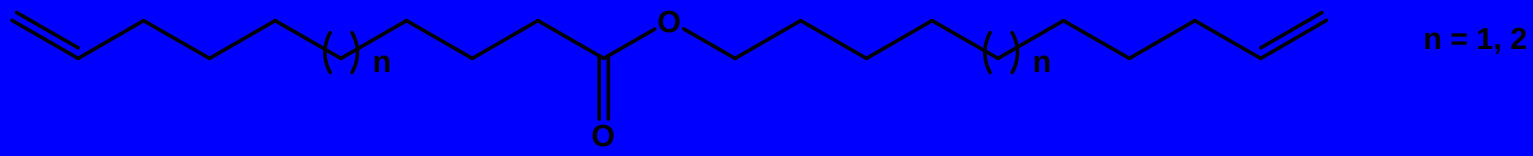
Kat.: B_2O_3 - Re_2O_7 / Al_2O_3 - SiO_2 + $SnMe_4$ or CH_3ReO_3 + B_2O_3 - Al_2O_3 - SiO_2

C18-, C20, C26-Dicarbonsäureester; Ausbeuten 77-84 %

S. Warwel, H.G. Jägers und S. Thomas, fat Sci. Technol. 94, 323 (1992)

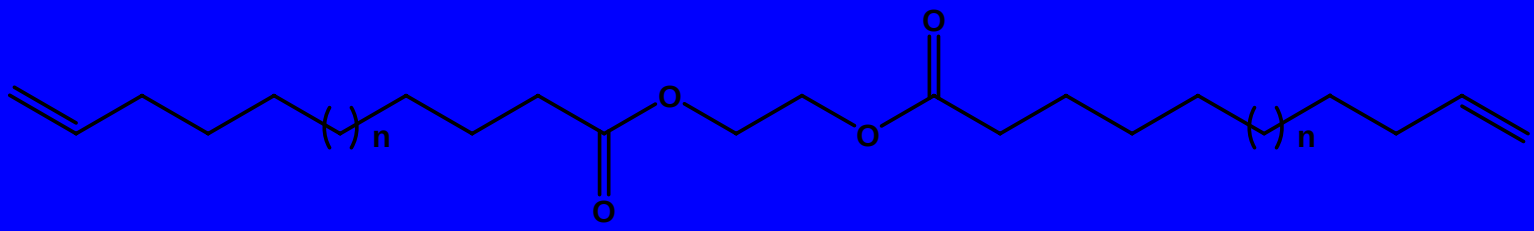
α,ω-ungesättigte Fettsäureester aus ω-ungesättigten Estern

- durch Umesterung mit dem Alkohol gleicher Kettenlänge

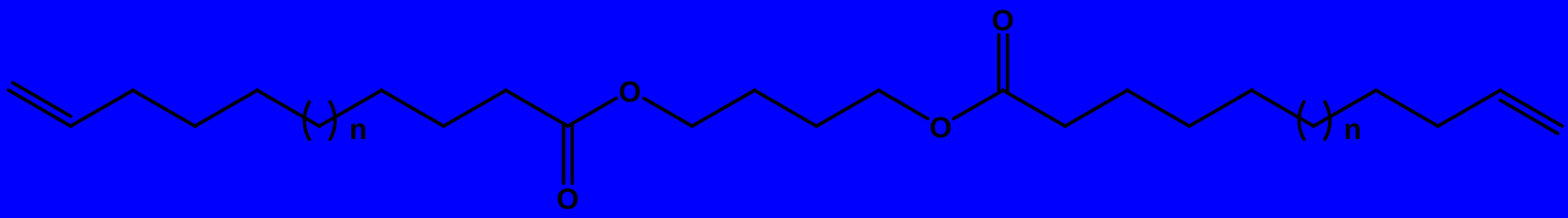


n = 1, 2

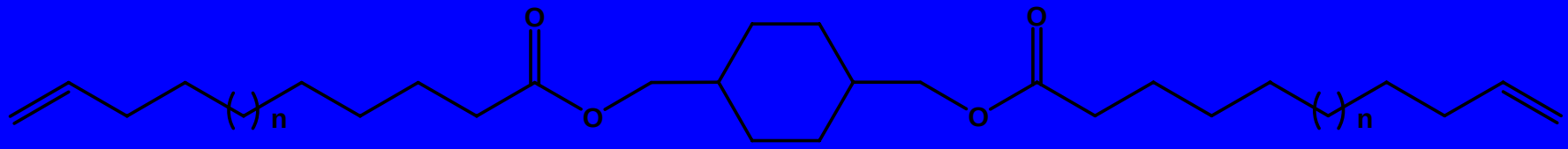
- durch Umesterung mit bifunktionellen Alkoholen petrochemischer Herkunft



n = 2

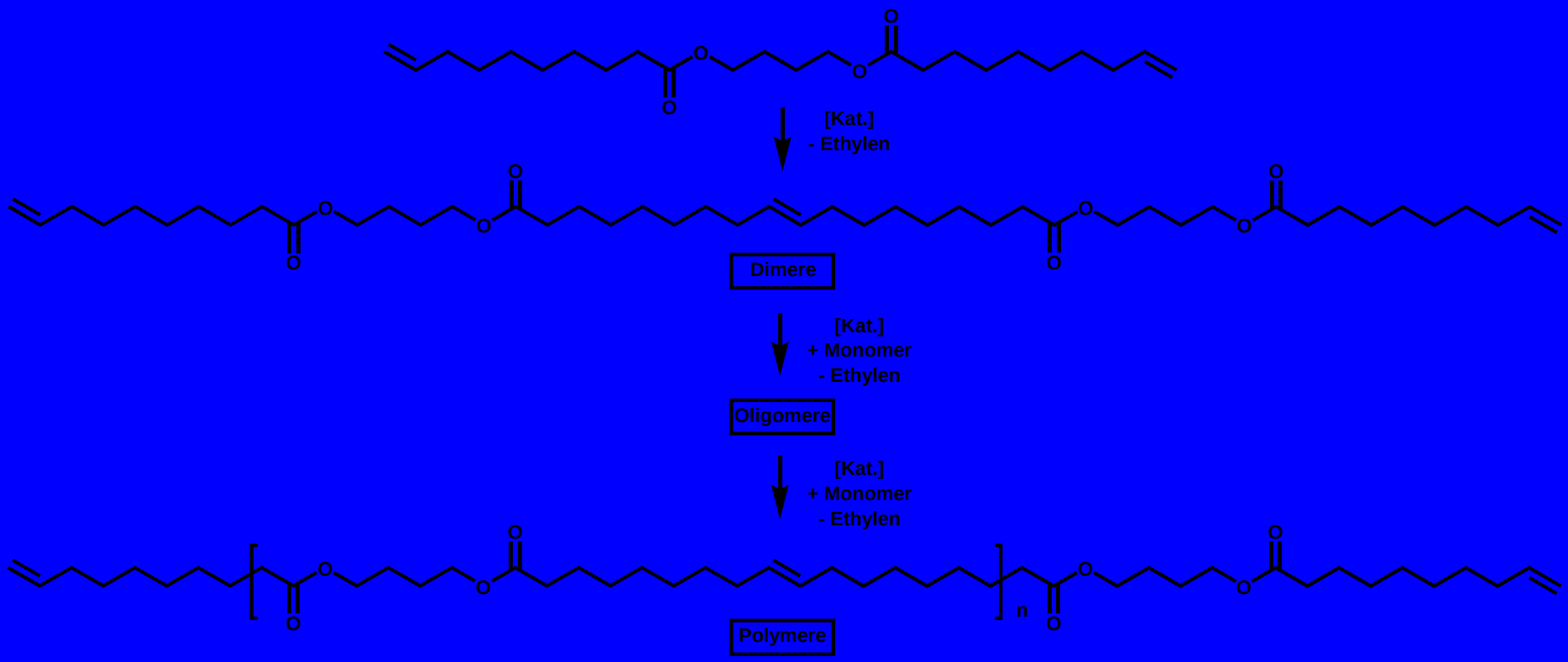


n = 1, 2



n = 1

Metathetische Polykondensation von 1,4-Butylendi-9-decenat

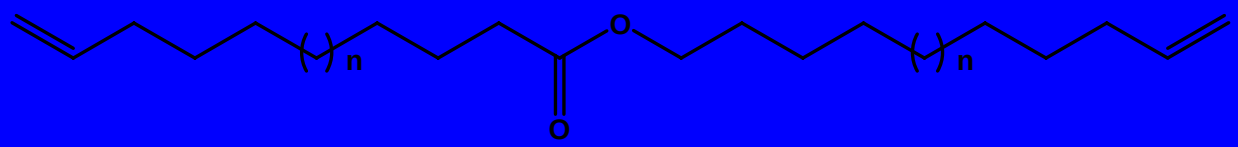


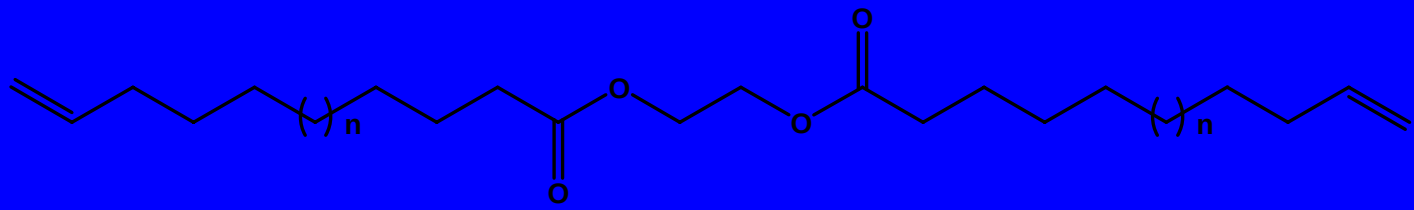
Mw = 99.800 g/mol

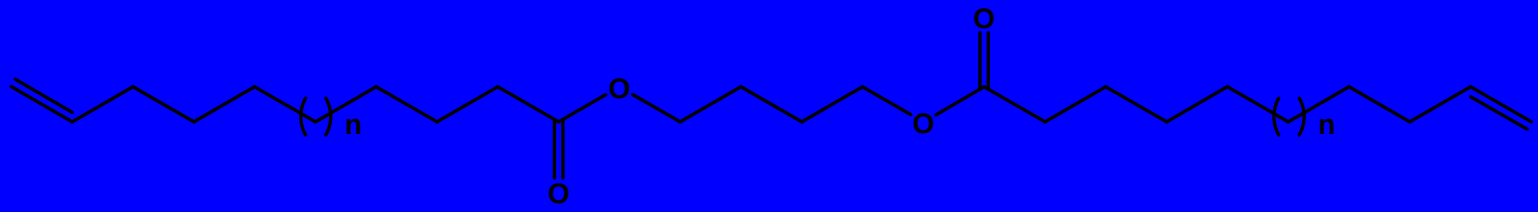
Katalysator: B_2O_3 - Re_2O_7 / Al_2O_3 - SiO_2 + $SnMe_4$

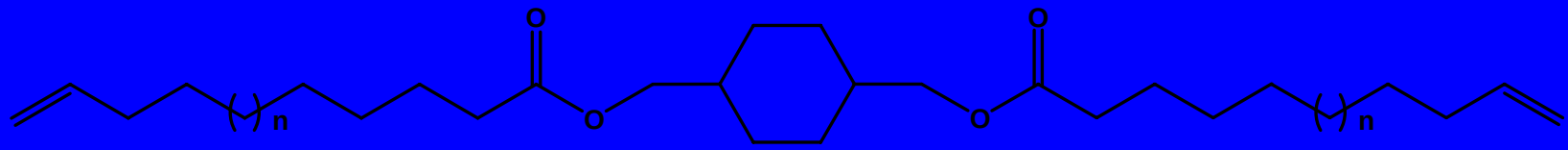
Bedingungen: 80°C, 24 h, 0.1 mbar Vakuum

Metathetische Polykondensation α,ω-ungesättigter Fettsäureester





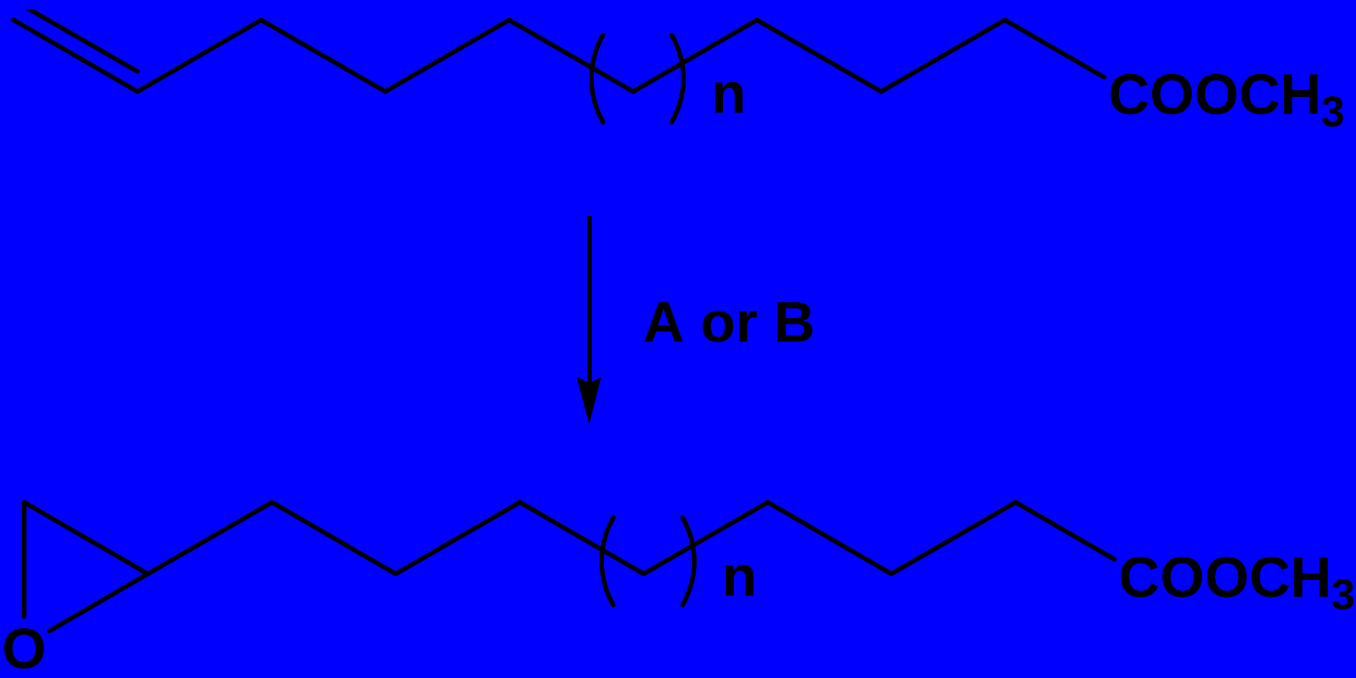




lineare, ungesättigte Polyester

Mw: 38.000 – 100.000 g/mol; Smp.: 36 - 70°C

Epoxidation ω-ungesättigter Fettsäureester



Ausbeuten: 70 - 90 %

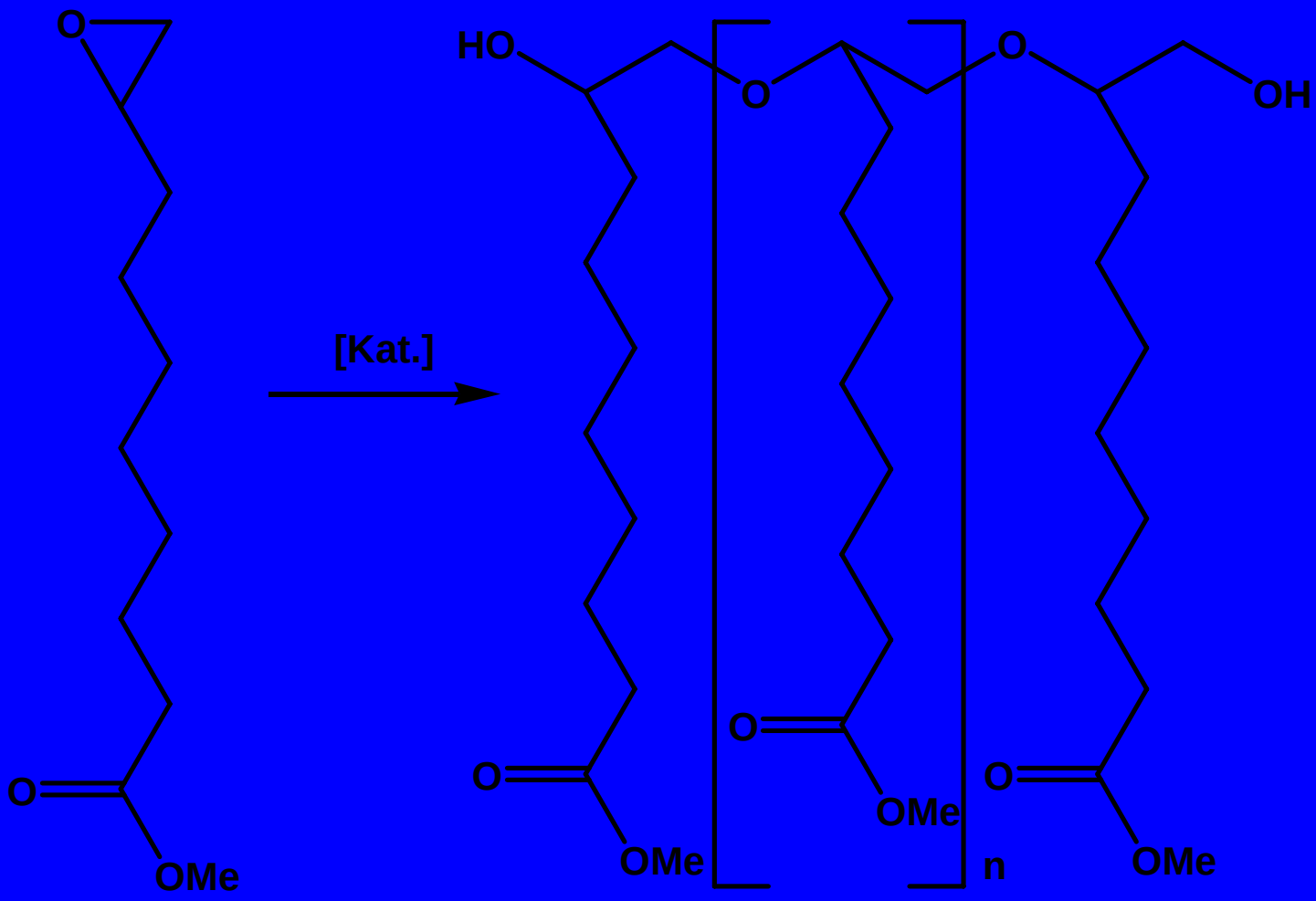
A: + CH_3CO_3H in $C_2H_4Cl_2$, RT

B: + H_2O_2, [Lipase], 40°C,

in Methylacetate oder Dimethylcarbonat

Fettchemische Polyether

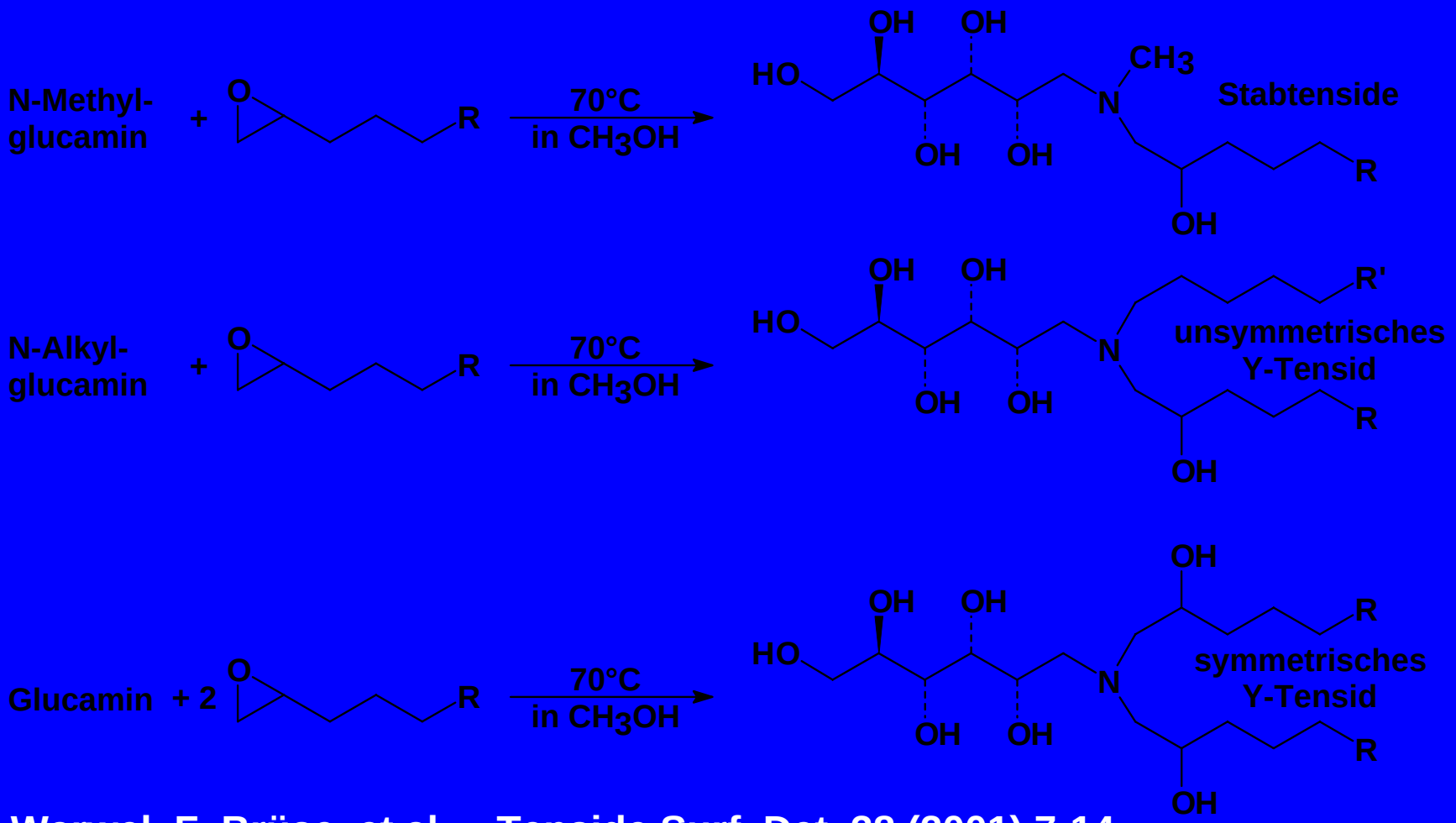
Kamm-Polymere aus fettchemischen Epoxiden



Kat.: Methylaluminoxan / Acetylaceton, Al / AcAc / Epoxide = 1 / 1 / 20 (molar)

100°C, 120 h, Toluol, Epoxide-Umsatz: 85 %, Mw: 435.000 g/mol

Strukturierte Kohlenhydrat – Tenside aus Zuckeraminen und endständigen Epoxiden

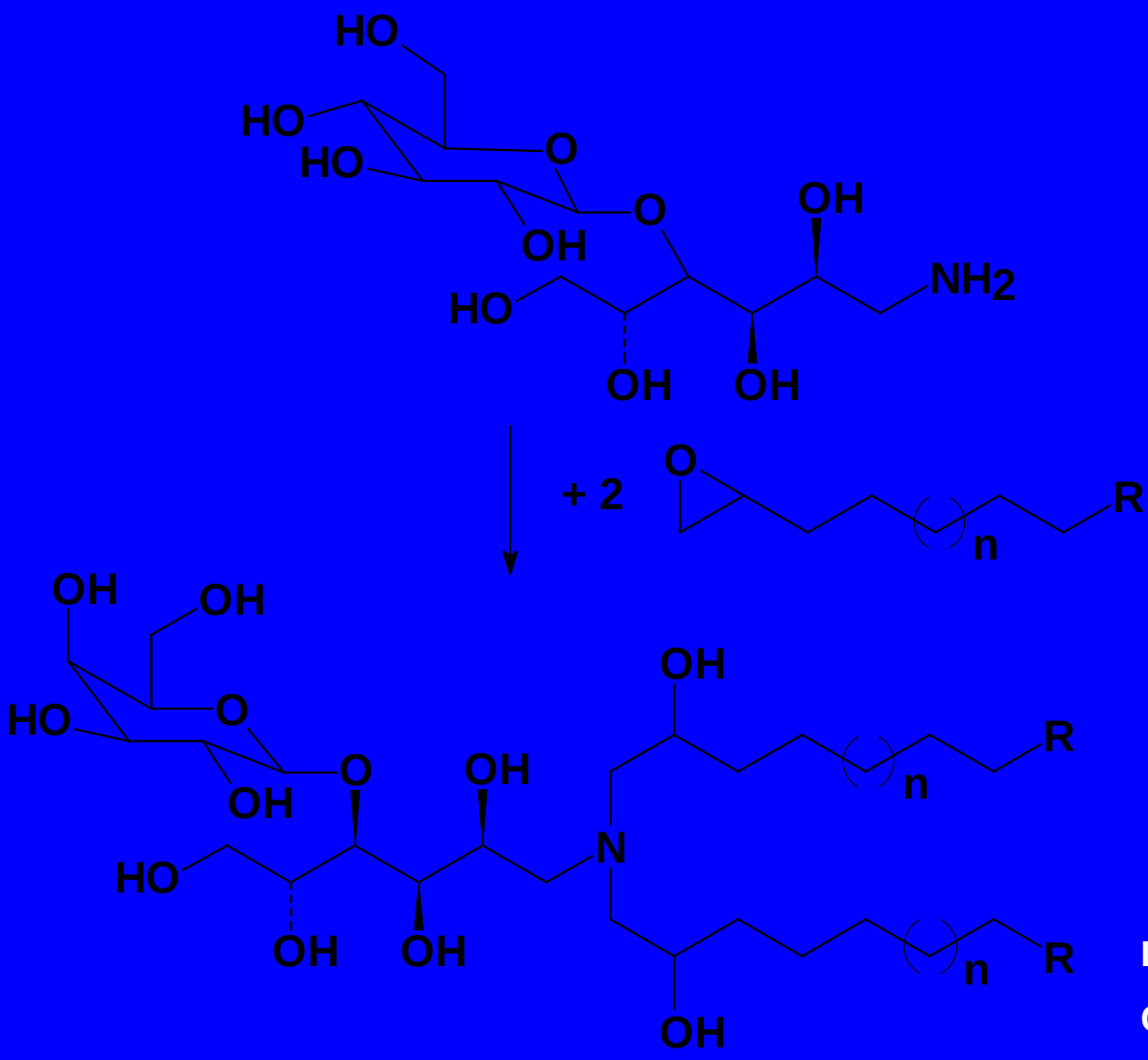


S. Warwel, F. Brüse, et al.: Tenside Surf. Det. 38 (2001) 7-14

Eur. J. Lipid Sci. Technol. 103 (2001) 645-654

Oleagineux Crops gras Lipides 8 (2001) 57-59

Zucker – Tenside auf Basis von Lactamin



R = CH_3; n = 1, 3, 5, 7, 9

R = $COOCH_3$; n = 3, 4, 7

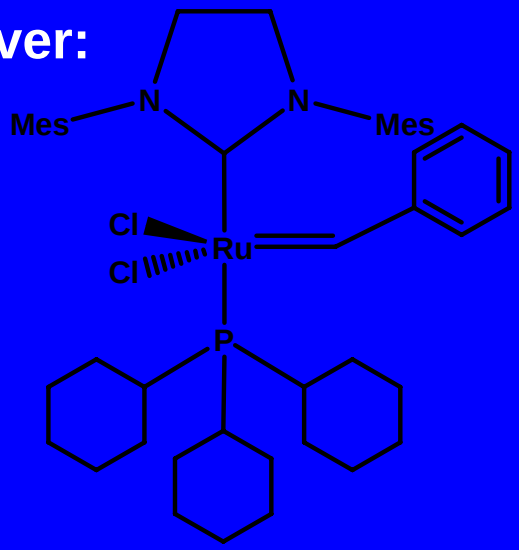
Löslichkeiten: 45-3400 mg/l

CMC: 1-500 mg/l;

OFS(γ): 25 - 38 mN/m

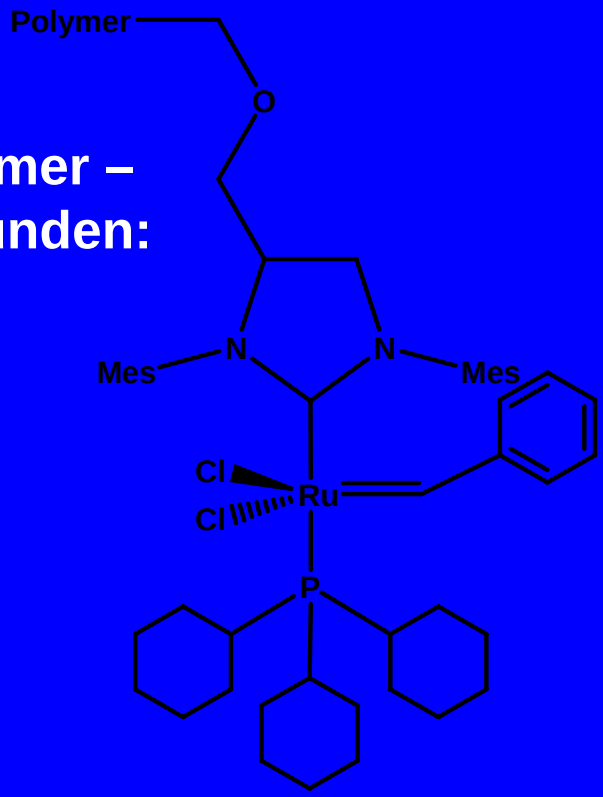
Neue Katalysatoren

Aktiver:



Mes = Mesityl

Polymer – gebunden:



Metathese mit ionischer Flüssigkeit als Katalysatorträger: