CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

ICMR
Institut de Chimie Moléculaire de Reims
UMR CNRS 6229

UNIVERSITÉ DE REIMS CHAMPAGNE-ARDENNE

Furfural Obtained from Pentoses – A Valuable Synthon for Fine Chemistry

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CNRS, Université de Reims
ICMR
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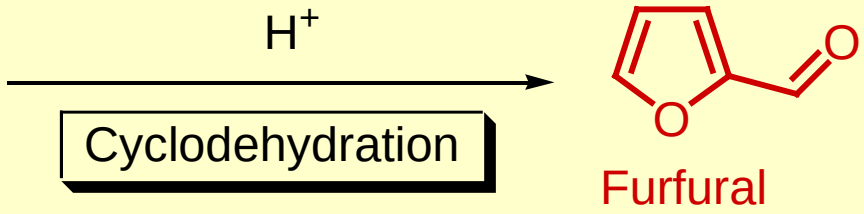
Reims, France

Production of Furfural

Pentose containing biomass, hemicelluloses



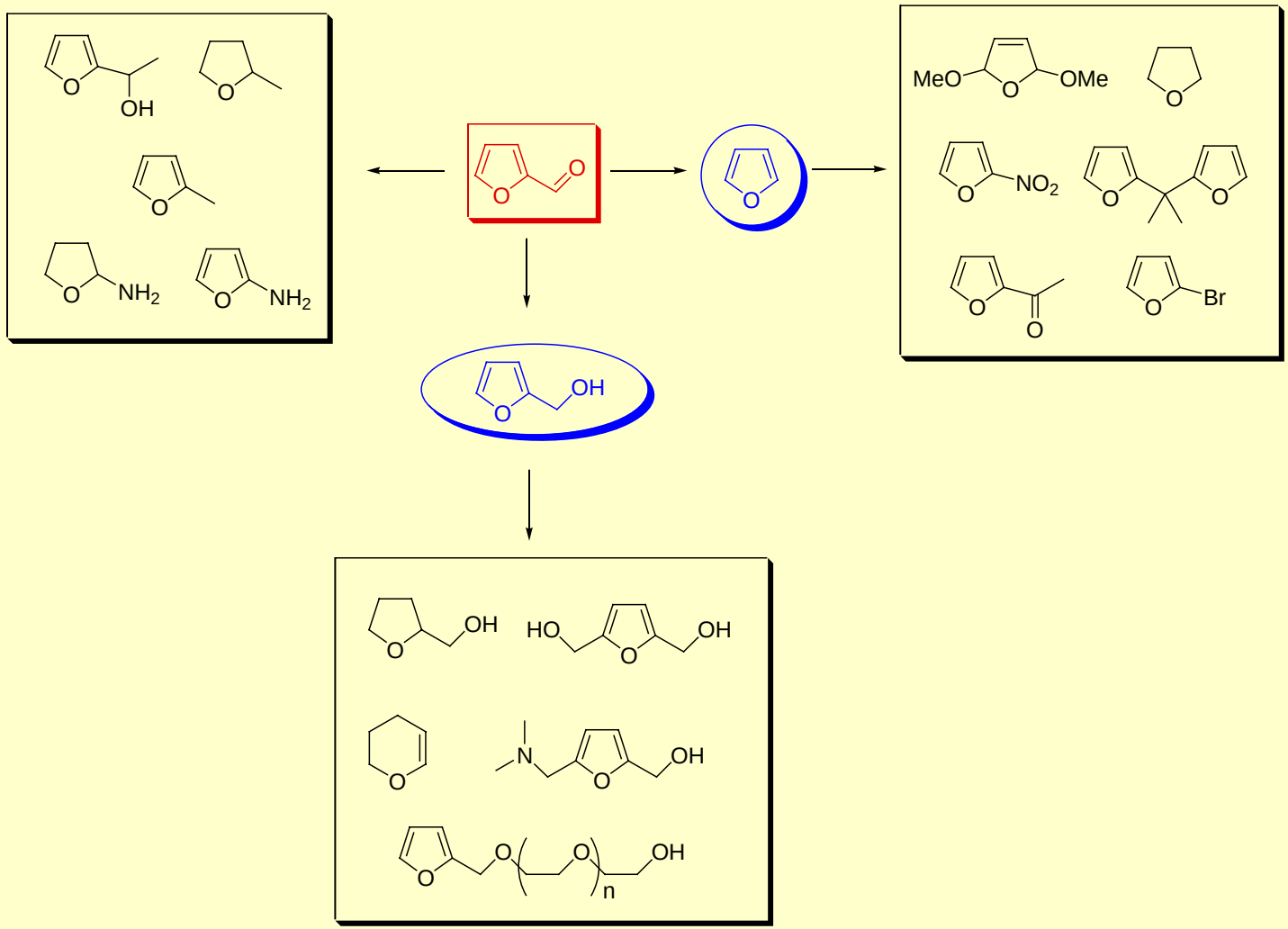
Worldwide production: > 280 000 tpa
Production in China: 200 000 tpa

J.-H. Hwang et al. *Biofuels, Bioprod. Bioref.* **2008**, *2*, 438.

B. Kamm, P. R. Gruber, M. Kamm (Eds.),
Biorefineries – Industrial Processes and Products. Wiley-VCH, Weinheim, **2006**.

J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2007**, *46*, 7164.

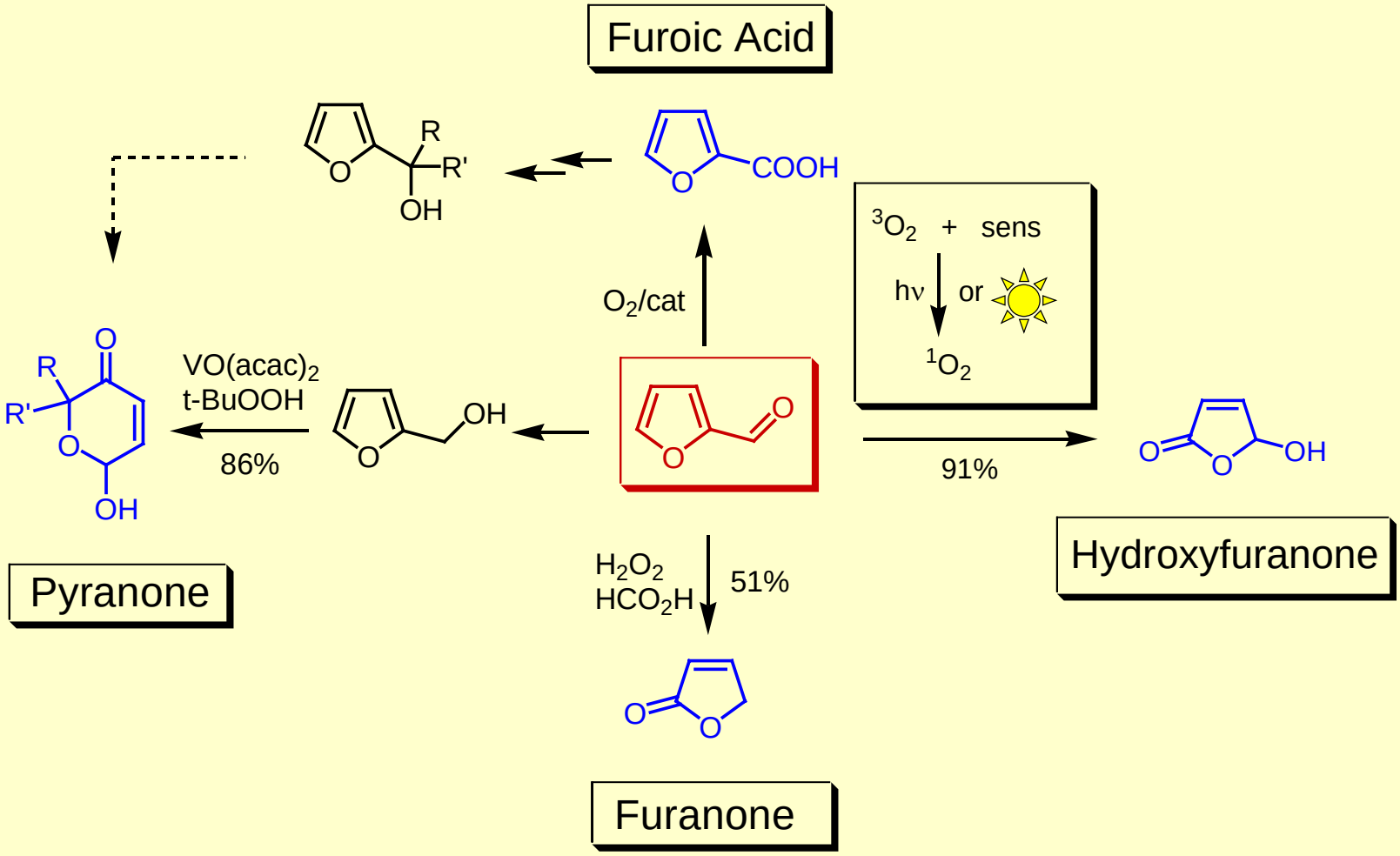
Reduction of Furfural



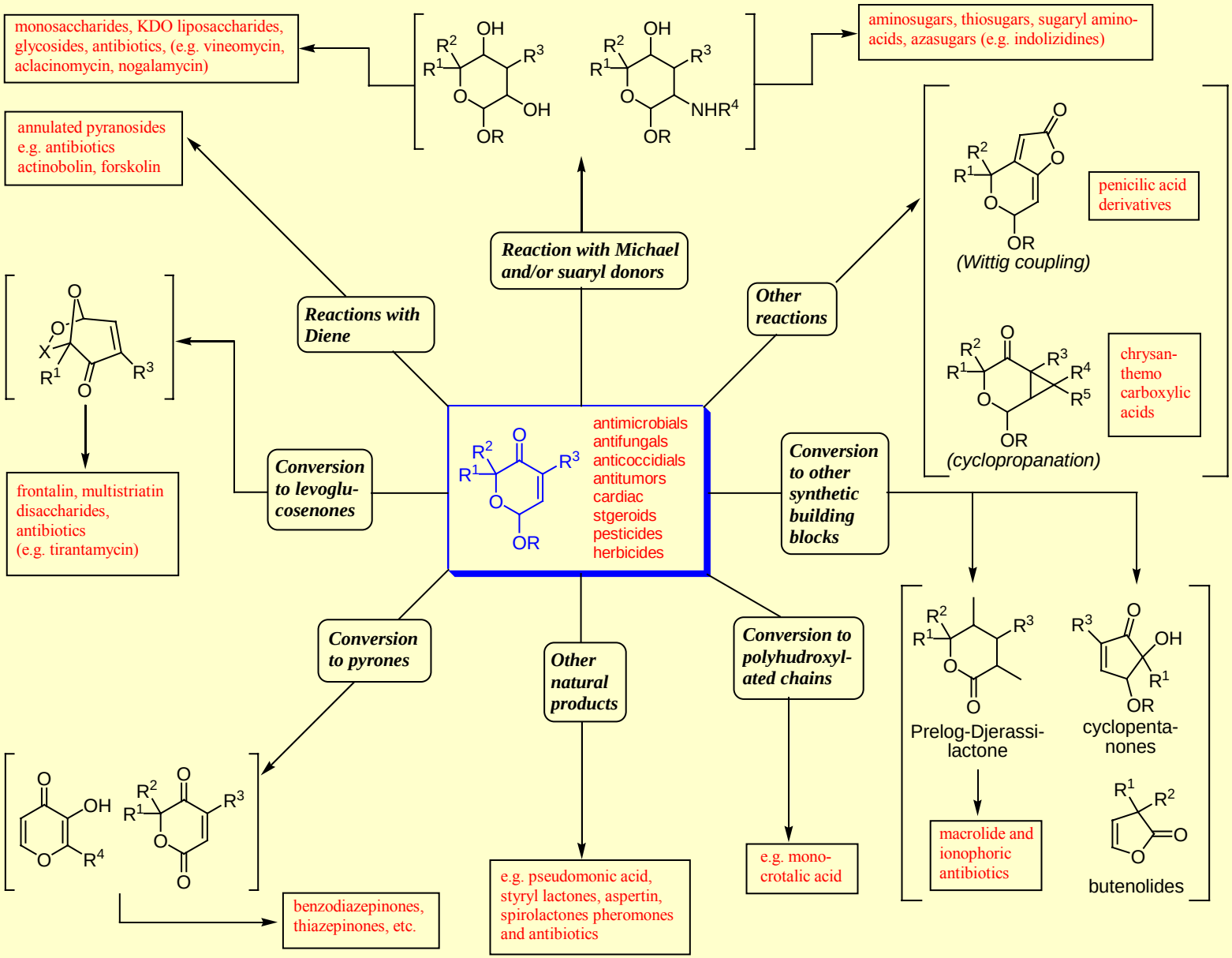
www.furan.com

J. N. Chheda, G. W. Huber, J. A. Dumesic,
Angew. Chem. Int. Ed. **2007**, *46*, 7164.

Oxydation of Furfural

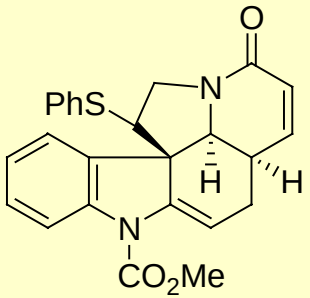


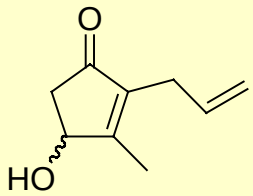
Pyranones as Versatile Synthons

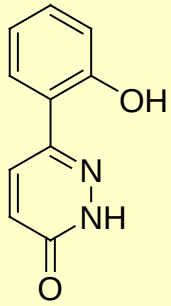


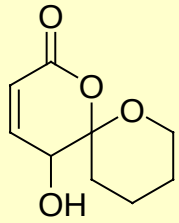
E. A. Couladouros, A. T. Strongilos, *Angew. Chem. Int. Ed.* **2002**, *41*, 3677

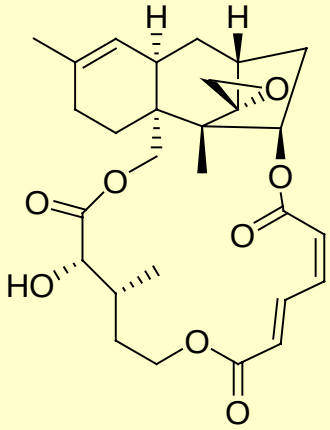
Hydroxyfuranone as a Versatile Synthon

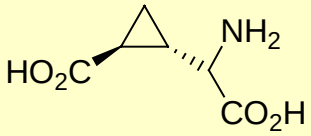


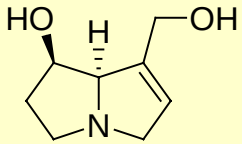


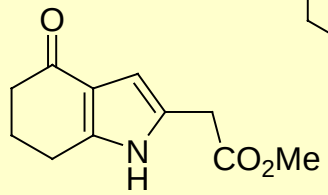


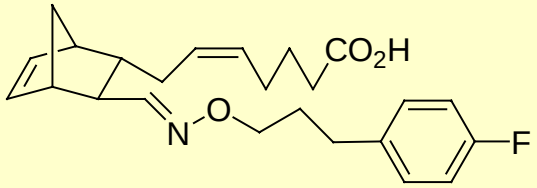


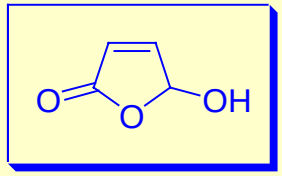


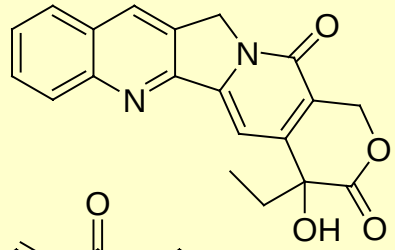


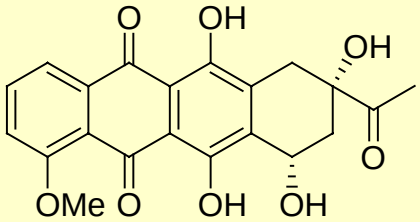


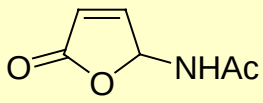


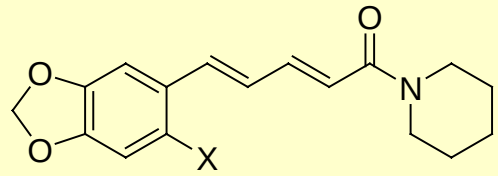


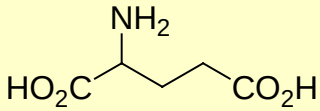




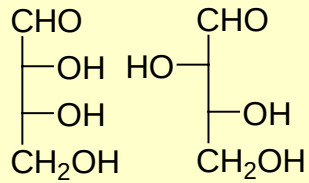




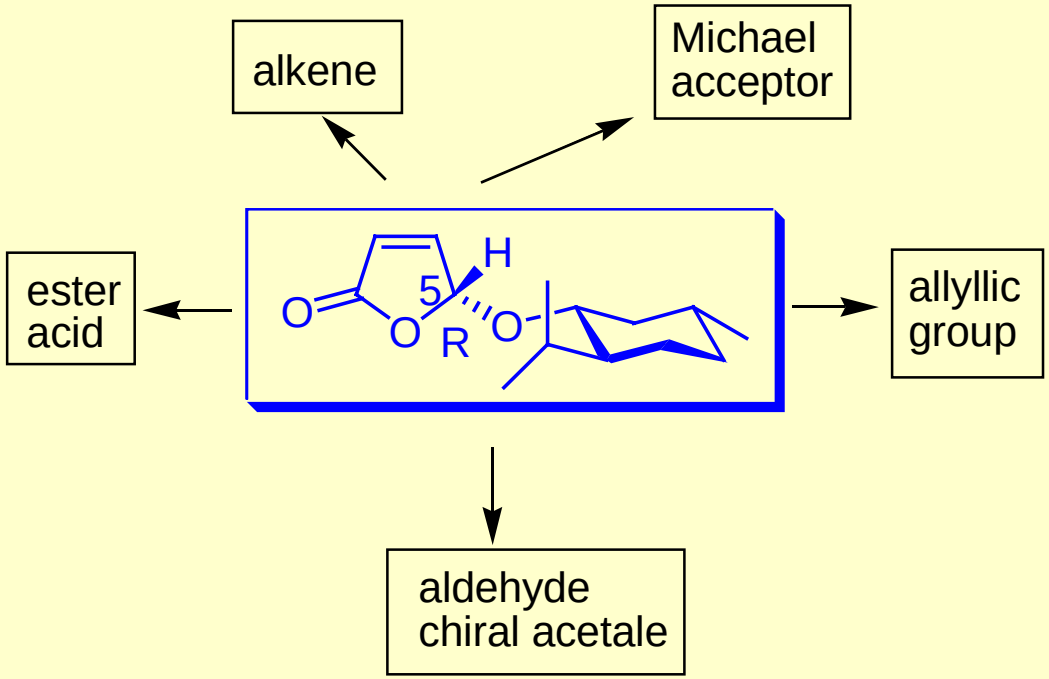




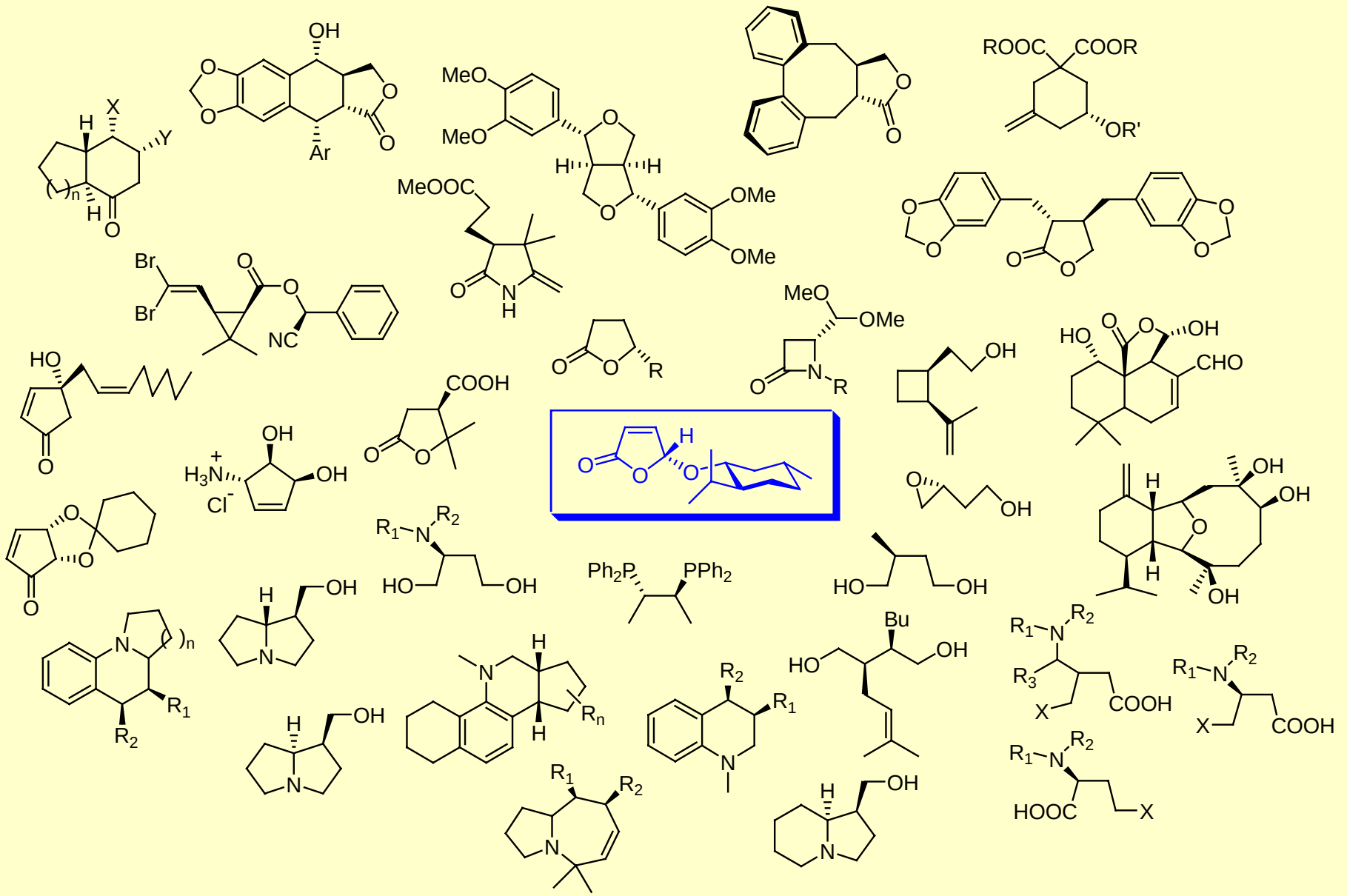
Insecticides, fungicides,
quick-drying varnishes



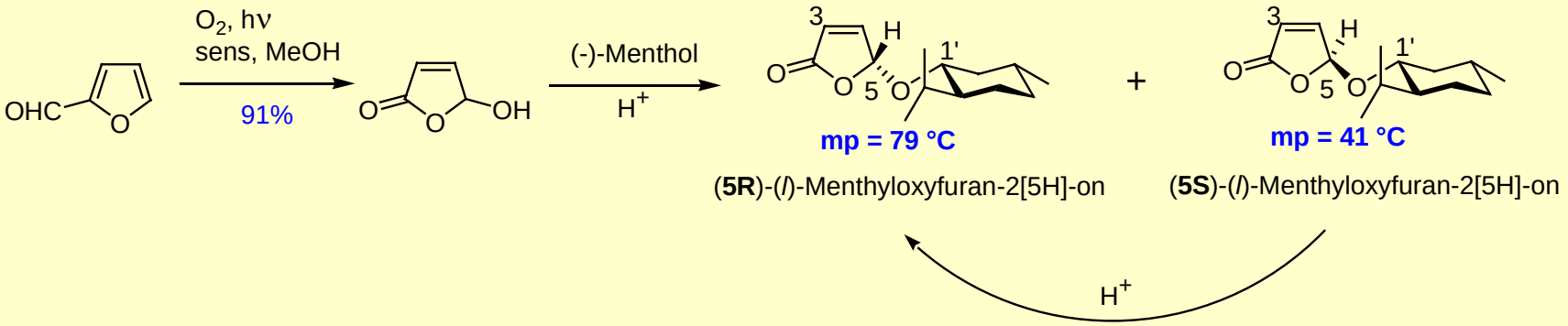
Menthyloxyfuranone as a Versatile Chiral Synthon

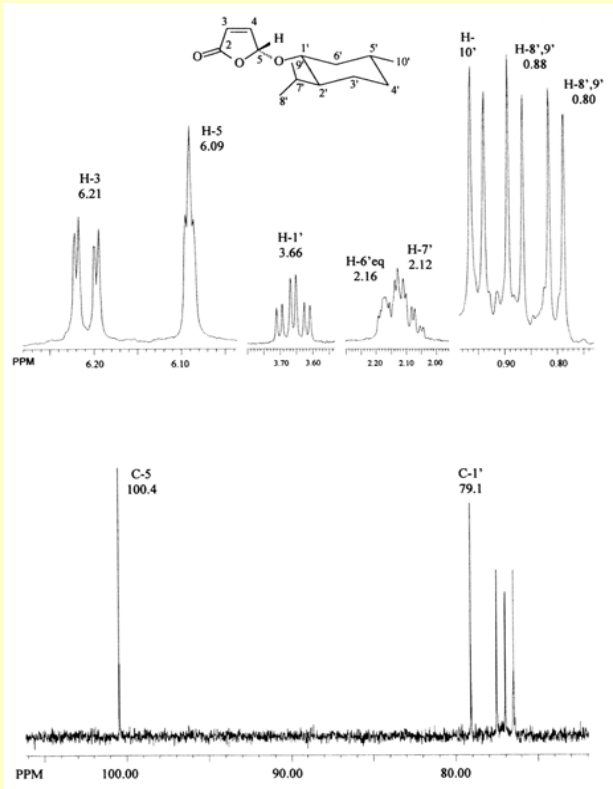


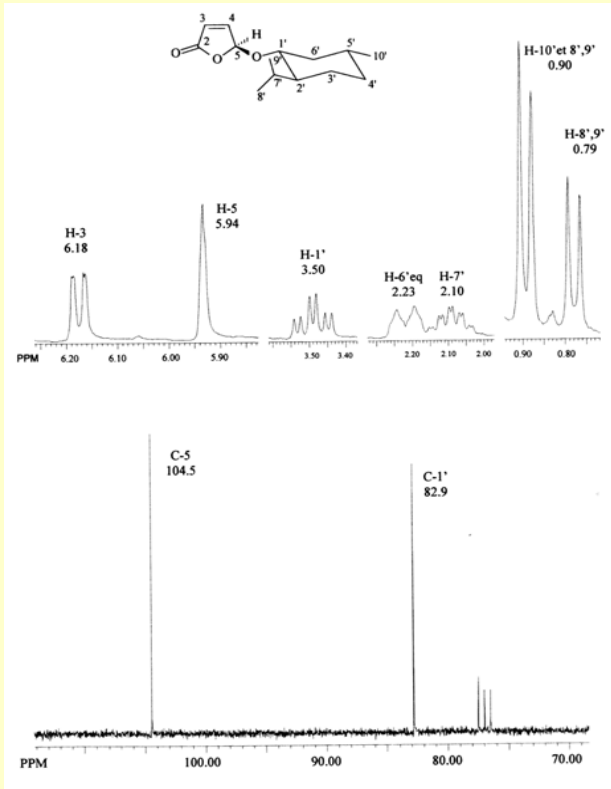
Menthyloxyfuranone as a Versatile Chiral Synthon



Synthesis of (5R)- and (5S)-((-)-Menthyloxy)-2[5H]-furanone

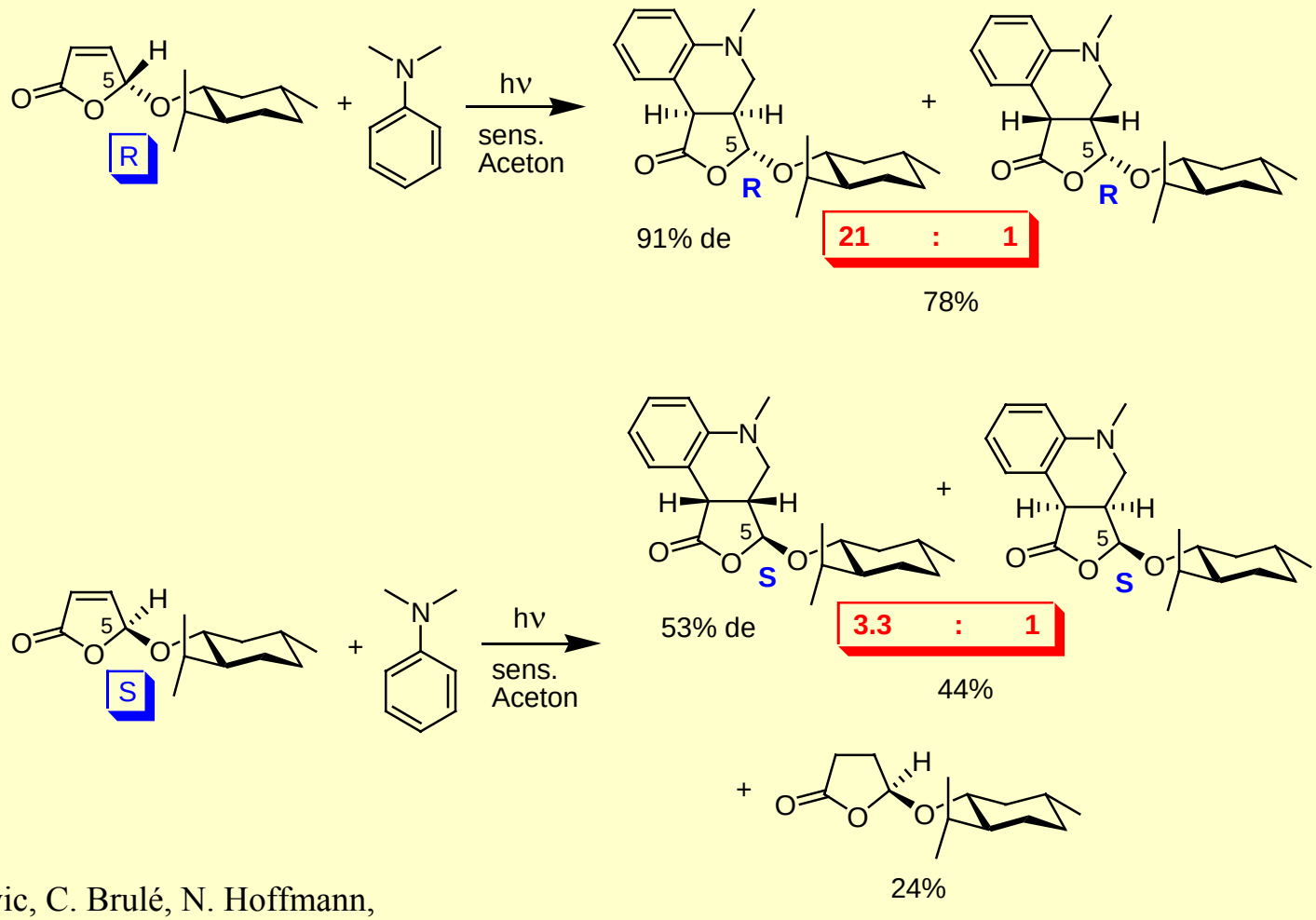






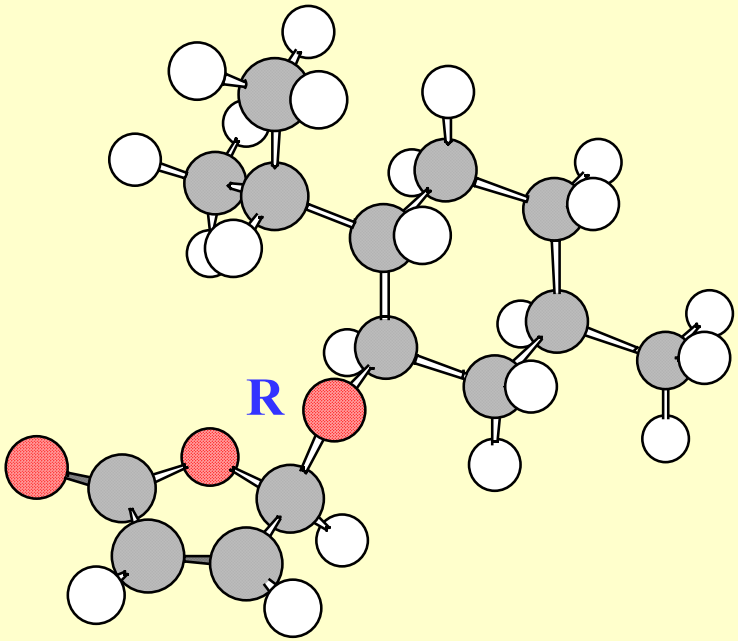
S. Marinkovic, C. Brulé, N. Hoffmann, E. Prost, J.-M. Nuzillard, V. Bulach, *J. Org. Chem.* **2004**, *69*, 1646

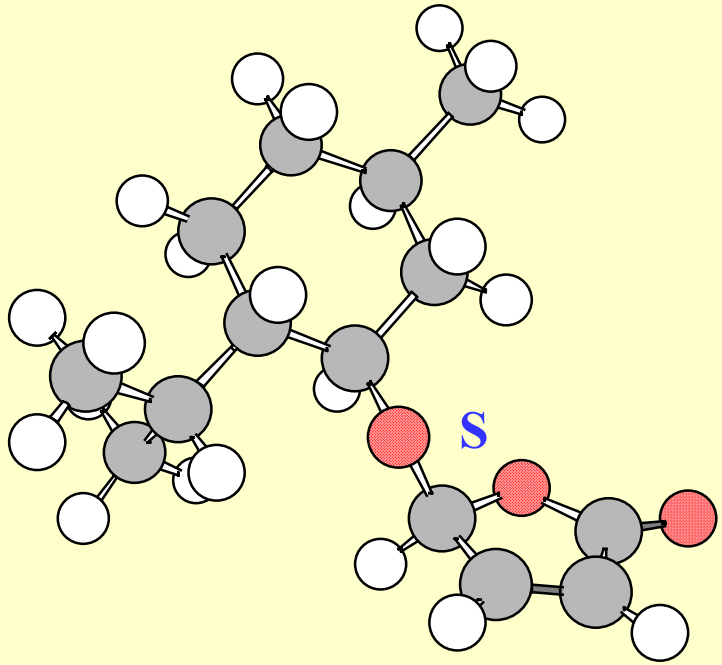
Radical-Tandem-Reaction with (5R)- and (5S)-((-)-Menthyloxy)-2[5H]-furanone



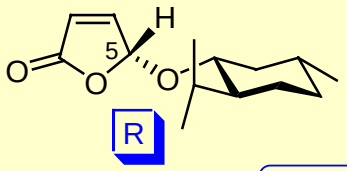
S. Marinkovic, C. Brulé, N. Hoffmann, E. Prost, J.-M. Nuzillard, V. Bulach, *J. Org. Chem.* **2004**, *69*, 1646

Conformation Analysis of
(5R)- and (5S)-((-)-Menthyloxy)-2[5H]-furanone



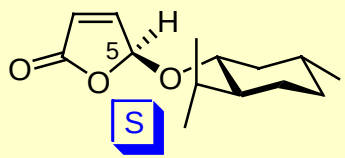


Double Induction with (5R)- and (5S)-((-)-Menthyloxy)-2[5H]-furanone



P(syn) / P(anti) : 21 / 1

Matched



P'(syn) / P'(anti) : 3 / 1

Mismatched

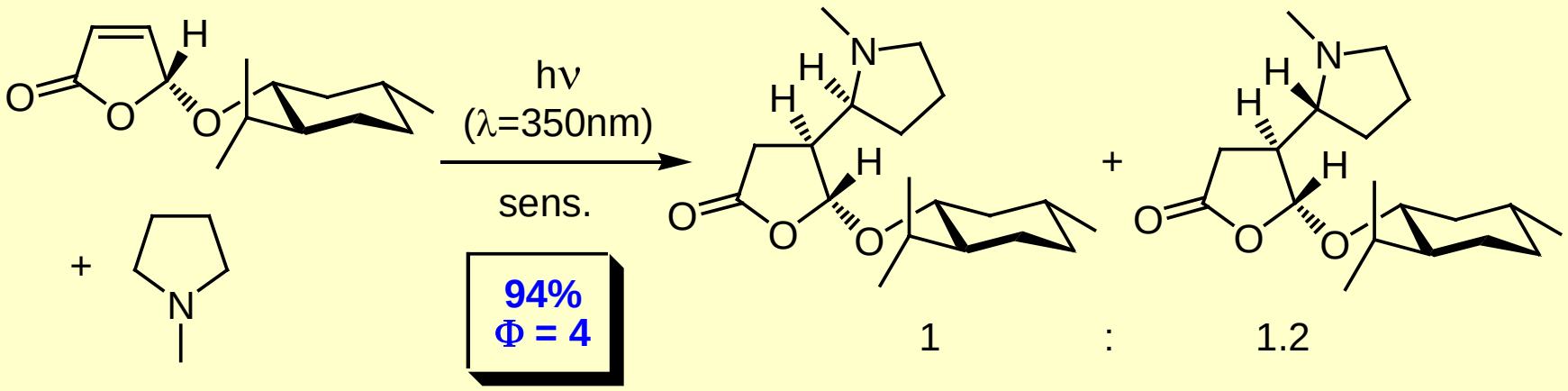
$$\ln (P(syn) / P(anti)) = -(\Delta\Delta G^{\neq}_{a} + \Delta\Delta G^{\neq}_{menth}) / RT$$

$$\ln (P'(syn) / P'(anti)) = -(\Delta\Delta G^{\neq}_{a} - \Delta\Delta G^{\neq}_{menth}) / RT$$

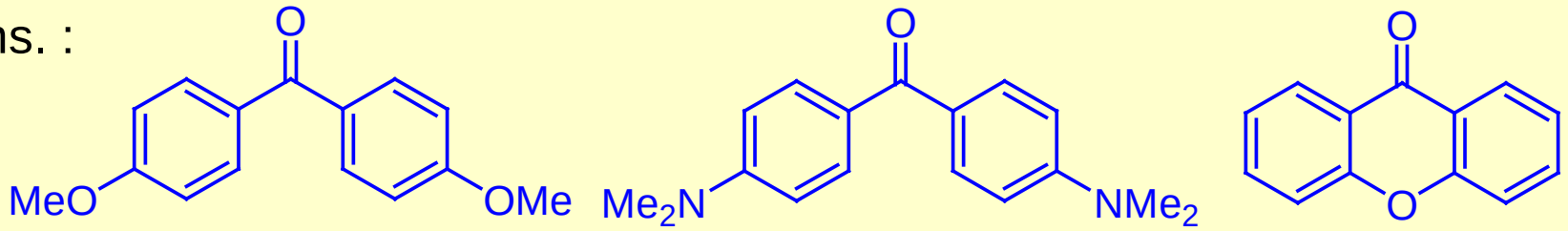
$$\Delta\Delta G^{\neq}_{a} = -1.24 \text{ kcal.mol}^{-1}$$

$$\Delta\Delta G^{\neq}_{menth} = -0.58 \text{ kcal.mol}^{-1}$$

Radical Addition of Tertiary Amines to Electron Deficient Alkenes



sens. :



S. Bertrand, N. Hoffmann, J.-P. Pete, *Eur. J. Org. Chem.* **2000**, 2227.

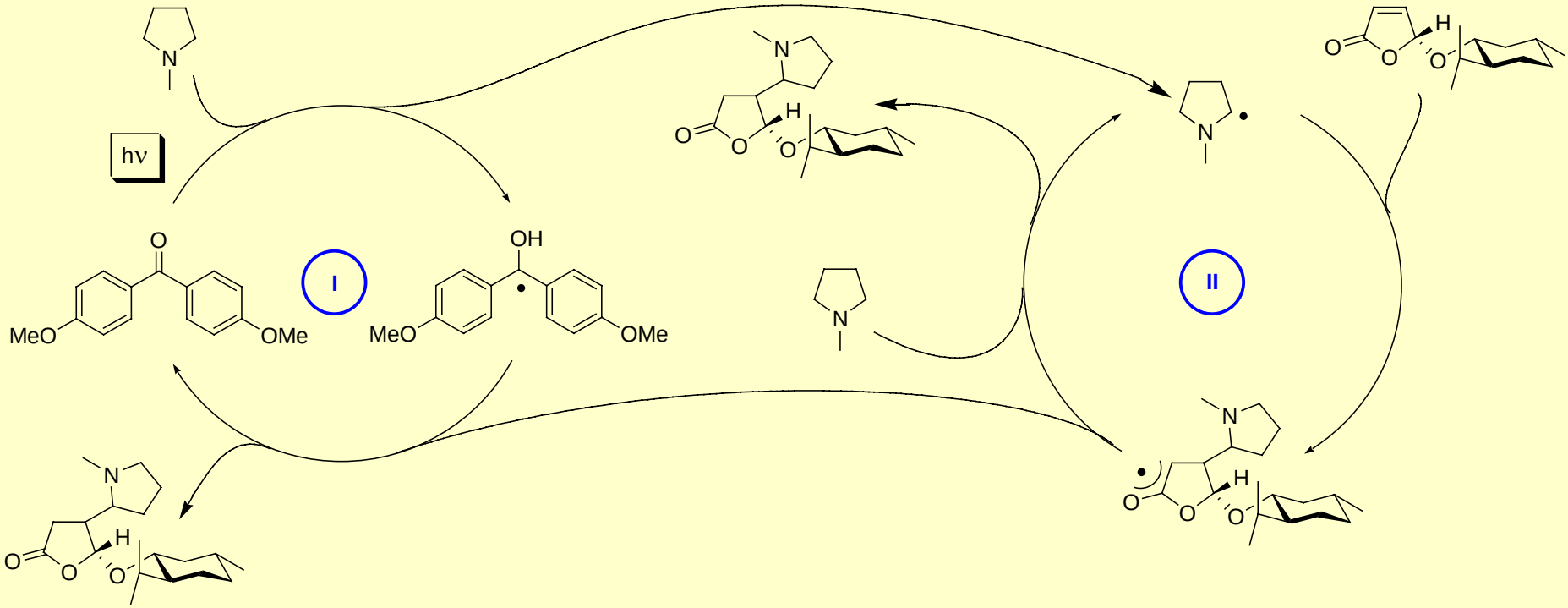
A. G. Griesbeck, N. Hoffmann, K.-D. Warzecha, *Acc. Chem. Res.* **2007**, *40*, 128

Comparing New and Conventional Sensitizers

New Sensitizers	Conventional Sensitizers (benzophenone, acetophenone)
High yields (>90%)	Modest yields (~40%)
Fast reactions (15g after 5min of irradiation)	Slow reactions
Catalytic amounts	At least stoechiometric amounts
Recovery up to 80% after the reaction	Degradation of the sensitizer
	Formation of many side products

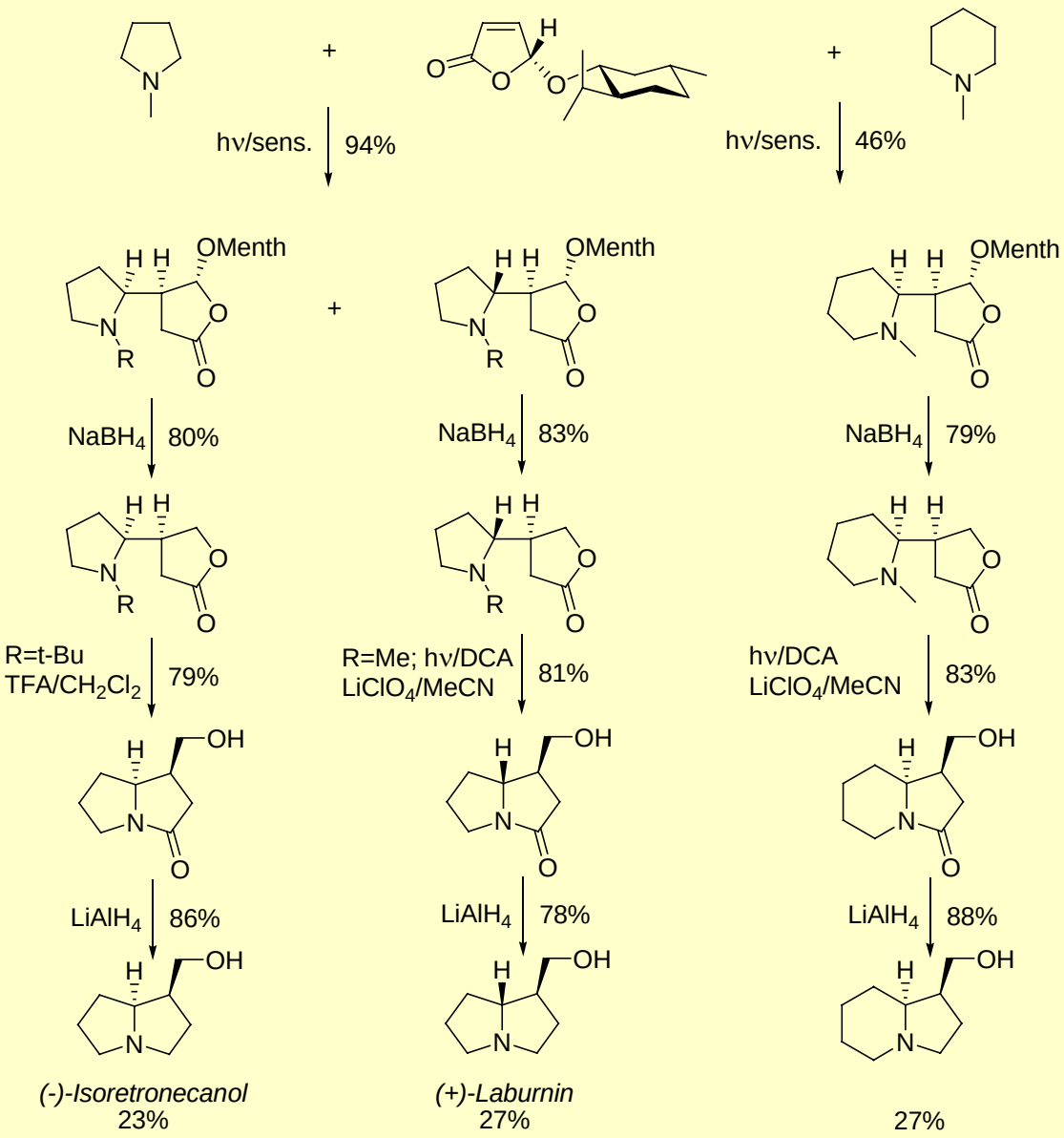
N. Hoffmann, *J. Photochem. Photobiol. C: Photochem. Rev.* **2008**, *9*, 43
See also: N. Hoffmann, H. Görner, *Chem. Phys. Lett.* **2004**, *383*, 451

Mechanism of the Radical Addition of tertiary Amines to Electron Deficient Alkenes



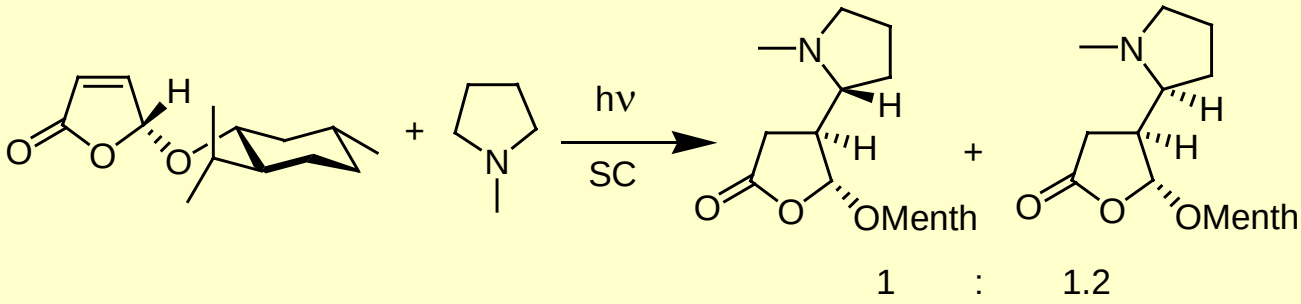
S. Bertrand, N. Hoffmann, J.-P. Pete, *Eur. J. Org. Chem.* **2000**, 2227.
See also: S. Bertrand, N. Hoffmann, S. Humbel, J.-P. Pete, *J. Org. Chem.* **2000**, *65*, 8690.
N. Hoffmann, *Chem. Rev.* **2008**, *108*, 1052.

Asymmetric Synthesis of Necines and Indolizidines



S. Bertrand, N. Hoffmann, J.-P. Pete, *Eur. J. Org. Chem.* **2000**, 2227.

Semiconductor Catalyzed Radical Addition of Tertiary Amines with Electron Deficient Alkenes

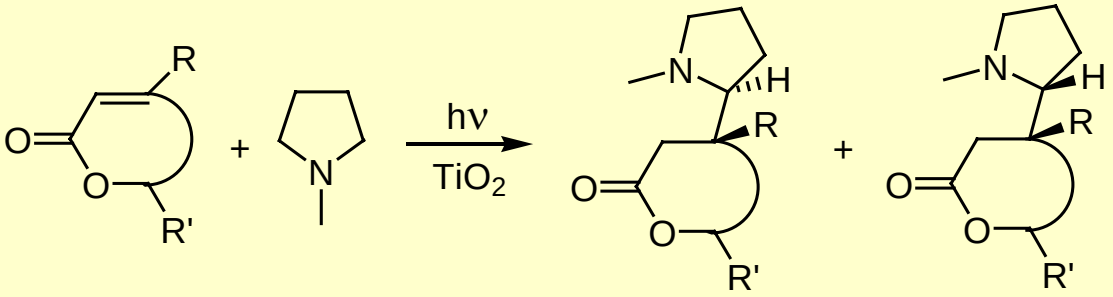


Semi-conductor [a]	c(furanone) [mol/L]	c(amine) [mol/L]	Time of Irradiation [h]	Conversion [%]	Yield[b] [%]
TiO_2	10^{-2}	4.10^{-1}	9	59	25
ZnS	10^{-2}	4.10^{-1}	9	68	28
TiO_2	10^{-2}	solvent	2.5	100	53
ZnS	10^{-2}	solvent	2.5	100	59
TiO_2	**5.10^{-2}**	**solvent**	**2.5**	**73**	***90***
TiO_2	10^{-1}	solvent	2.5	50	39

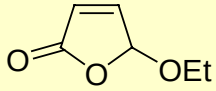
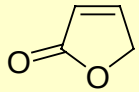
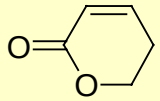
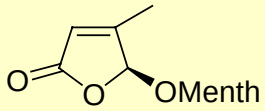
[a] 2 mol-% with respect to the furanone.
[b] Based on conversion of the furanone.

S. Marinkovic, N. Hoffmann, *Chem. Commun.* **2001**, 1576
S. Marinkovic, N. Hoffmann, *Intern. J. Photoenergy* **2003**, 5, 175

Semiconductor Catalyzed Radical Addition of Tertiary Amines with Electron Deficient Alkenes



1 : 1.2

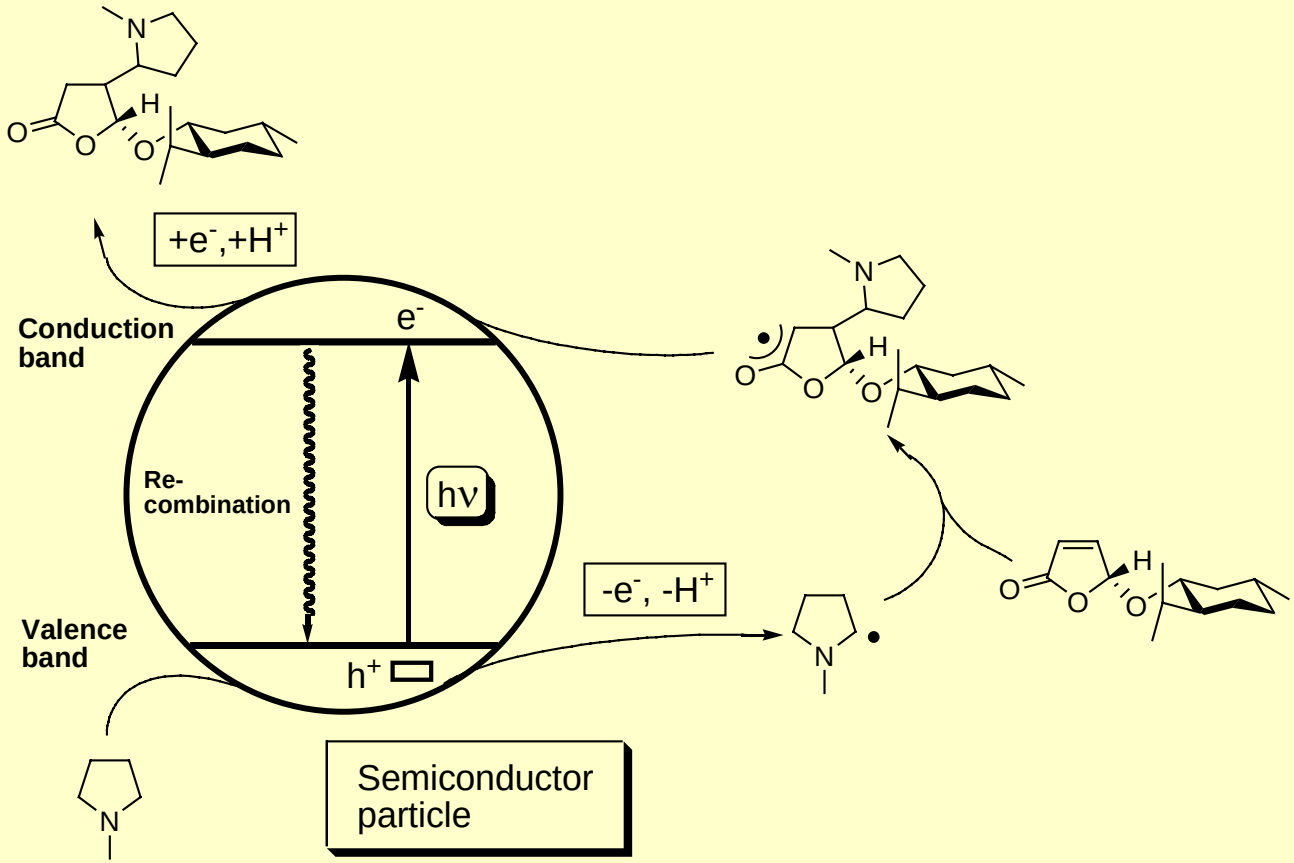
	Time of Irradiation [h]	Conversion [%]	Yield[a] [%]
	2	90	64
	**2**	**100**	***98***
 [b]	3.5	100	90
	13	20	76

[a] Based on conversion of the α,β-unsaturated lactone.

[b] The starting concentration was 10^{-2} mol/L.

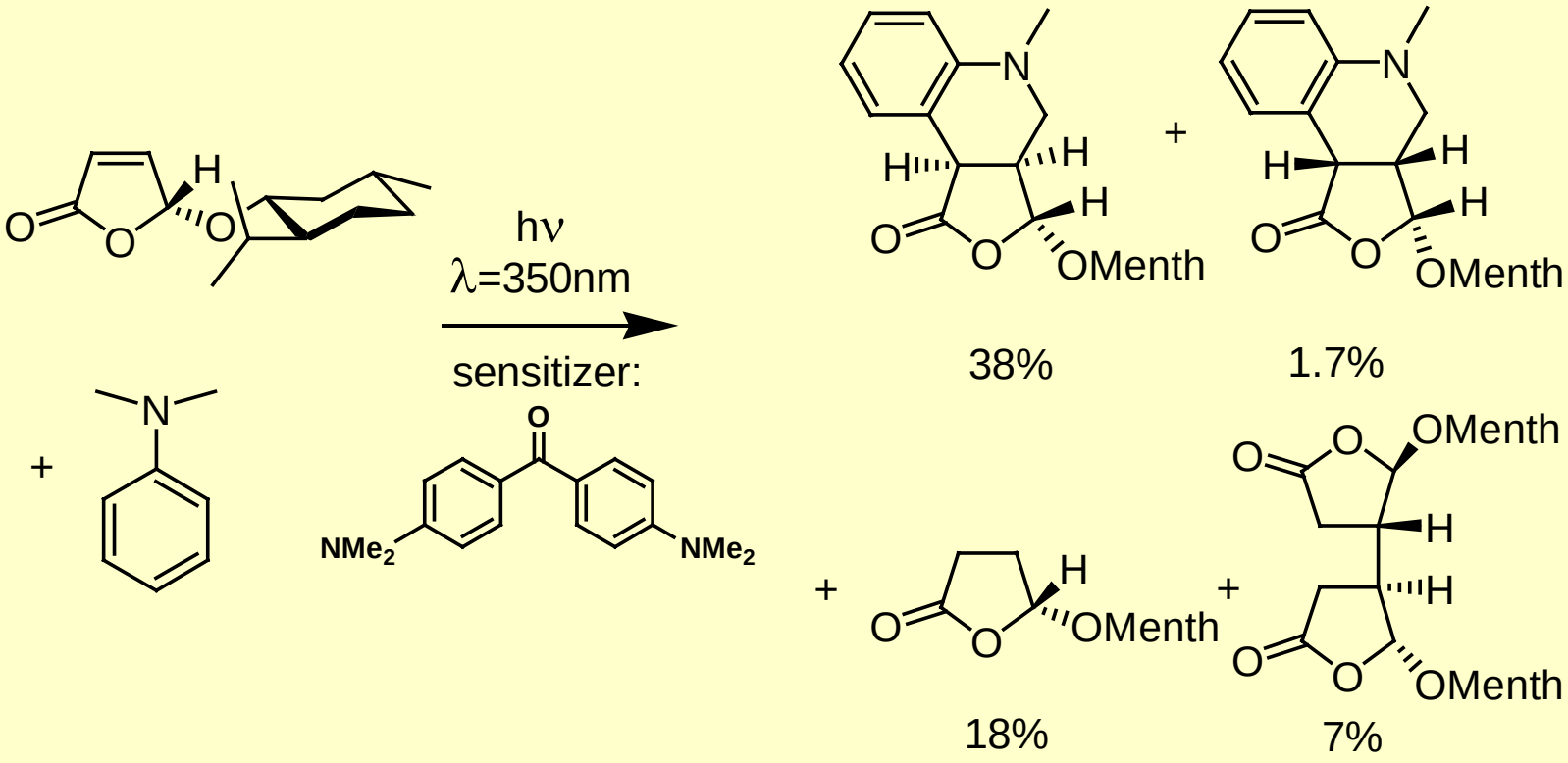
S. Marinkovic, N. Hoffmann, *Chem. Commun.* **2001**, 1576
S. Marinkovic, N. Hoffmann, *Intern. J. Photoenergy* **2003**, *5*, 175

Mechanism of the Semiconductor Catalyzed Radical Addition of Tertiary Amines with Alkenes

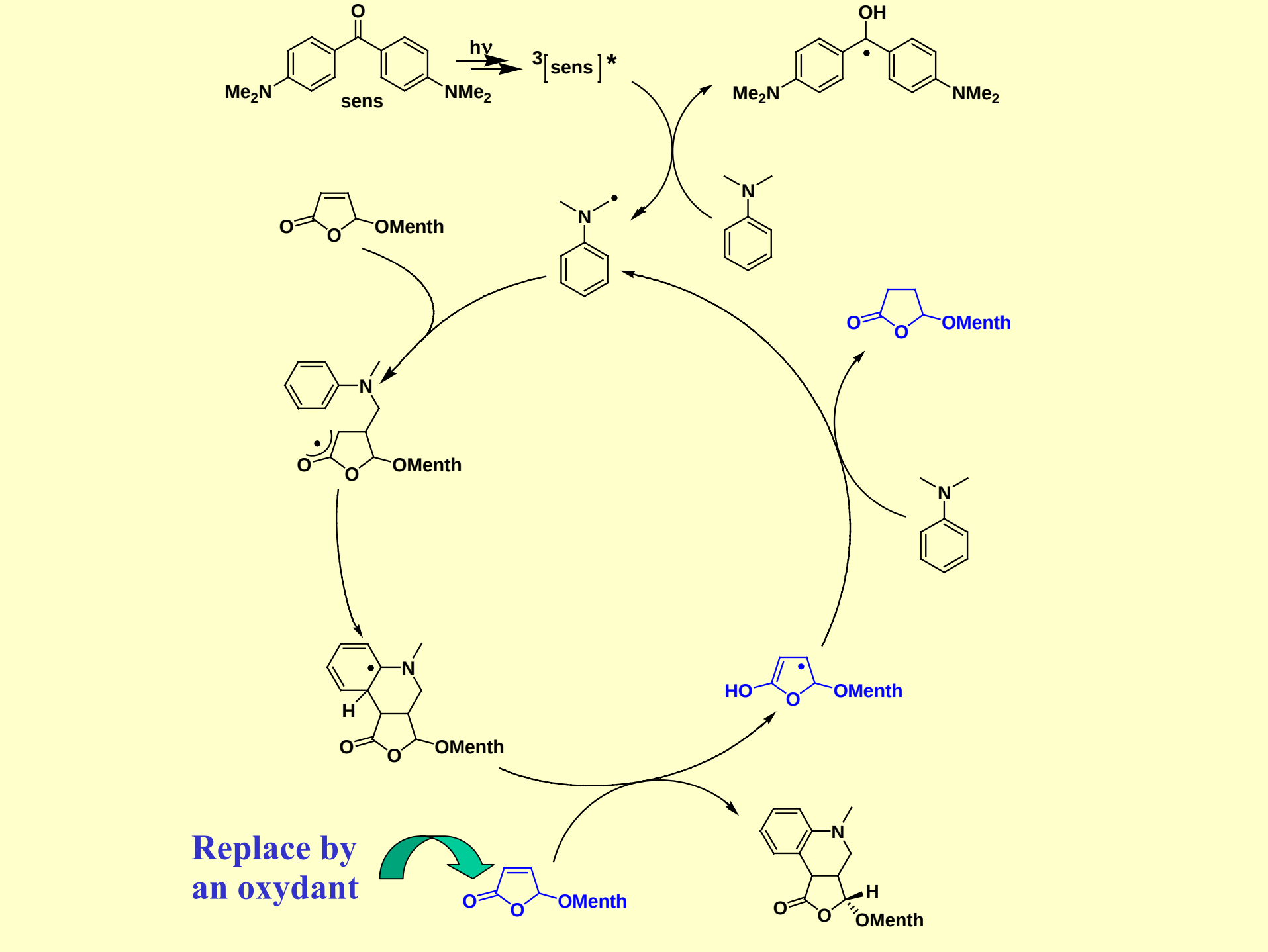


S. Marinkovic, N. Hoffmann, *Chem. Commun.* **2001**, 1576
S. Marinkovic, N. Hoffmann, *Intern. J. Photoenergy* **2003**, *5*, 175

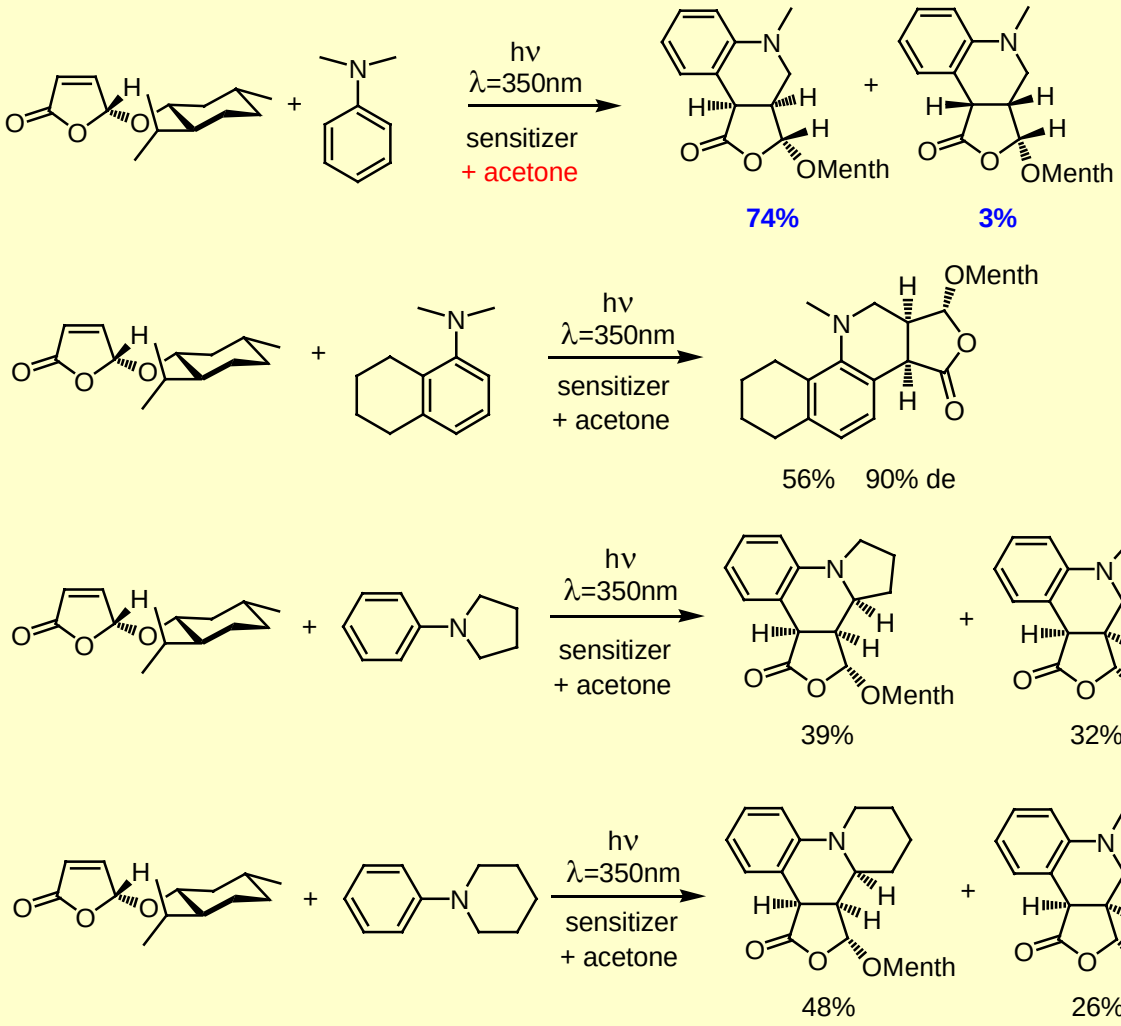
Radical Tandem Reaction of Aromatic Tertiary Amines with Electron Deficient Alkenes



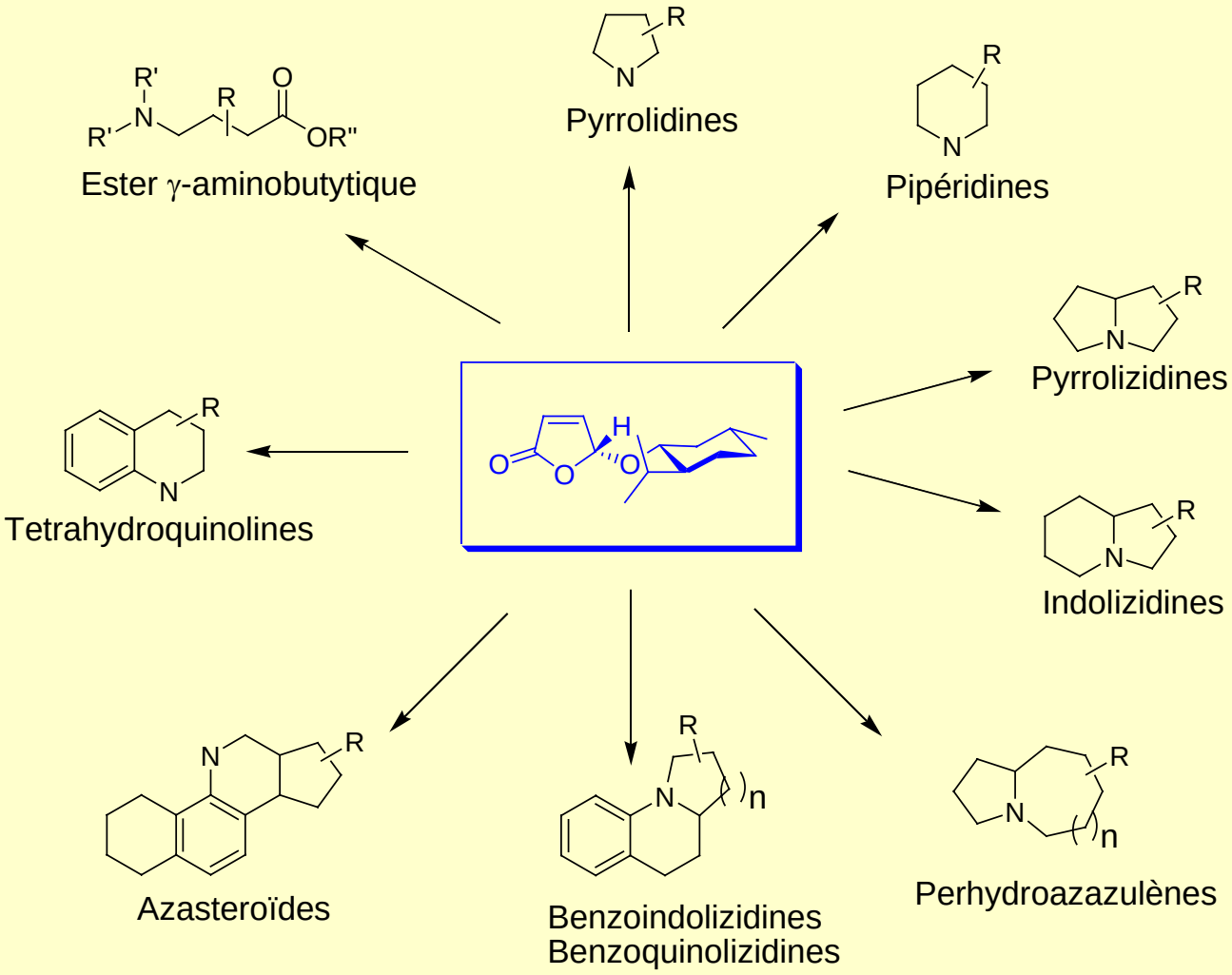
S. Bertrand, N. Hoffmann, S. Humbel, J.-P. Pete, *J. Org. Chem.* **2000**, *65*, 8690
N. Hoffmann, S. Bertrand, S. Marinkovic, J. Pesch, *Pure Appl. Chem.* **2006**, *78*, 2227


hν
3[sens]*
sens
Me2N
NMe2
OH
OMenth
HO
Replace by
an oxydant

Radical Tandem Reaction of Aromatic Tertiary Amines with Electron Deficient Alkenes



S. Bertrand, N. Hoffmann, S. Humbel, J.-P. Pete, *J. Org. Chem.* **2000**, *65*, 8690


Ester γ-aminobutytique
Pyrrolidines
Pipéridines
Pyrrolizidines
Indolizidines
Perhydroazazulènes
Benzoindolizidines
Benzoquinolizidines
Azasteroïdes
Tetrahydroquinolines

Conclusions

Furfural obtained from pentose containing biomass is a ***versatile synthon for the production*** of a ***large variety of fine chemicals***

Key intermediates are obtained by ***reduction and oxidation of furfural***.

Hydroxyfuranones obtained by ***photochemical oxidation of furfural*** can easily be transformed into numerous ***biologically active target compounds*** such as nitrogen containing heterocycles.

Transformations of products such as furfural from renewable resources in combination with environmentally friendly processes such as photochemical reactions provide perspectives for a sustainable chemical industry.

Thanks

Dr. Emmanuel Riguet

Dr. Samuel Bertrand
Dr. Céline Verrat
Dr. Siniša Marinković
Dr. Jens Pesch
Dr. Abdoulaye Gassama
Ali Youssef
Rabih Jahjah Hussein
Mathieu Queste
Dr. Frédéric Dumur
Dr. Frédéric Canonne
Dr. Cédric Brulé
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